



Tungsten as a hydrodenitrogenation catalyst for petroleum oil fractions
by Arthur Yngve Falk

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
© Copyright by Arthur Yngve Falk (1967)

Abstract:

The catalytic hydrodenitrogenation of high nitrogen content petroleum gas oils was studied. The primary objective of this research was to discover and/or develop a catalyst which could effectively remove nitrogen from high nitrogen content petroleum gas oils. A catalyst was sought which would be more effective at removing the nitrogen from the gas oil than the present commercially used cobalt/nickel molybdate catalysts.

The study was carried out on a bench scale, continuous, tubular flow reactor. The operating conditions utilized during this study were: temperature 700 to 820°F, pressure 1000 psig, hydrogen flow rate of 5000 SCF/ bbl. of oil, space velocity (L.H.S.V.) 0.25 to 2.0 ml. of oil/hour/ml. of catalyst. (In order for the hydrodenitrogenation process to be economically as well as technically sound, the pressure was limited to no greater than 1000 psig.) The primary feedstock source was the Santa Maria (California) crude source. The feedstocks, whose boiling ranges were approximately 550°F to 900°F, contained between 0.181 and 0.335 wt.% nitrogen.

All nitrogen conversion calculations were based on the total nitrogen concentrations determined by the Boyd Guthrie modification of the Kjeldahl method. A nickel-tungsten type catalyst, on a silica-alumina support, more active than the present commercially used cobalt/nickel molybdate hydrodenitrogenation catalyst's was developed. Use of a silica-alumina support, containing 5 to 7 percent silica (SiO₂) by weight, was found to result in a more active catalyst than a similar catalyst on an alumina support. Of the conventional hydrotreating catalyst promoters (nickel, cobalt, and molybdenum), nickel was found to be the most effective promoter for the tungsten type hydrotreating catalyst. The catalyst was found to be more effective (active) if properly sulfided prior to use.

As expected, the developed catalysts' activity decreased with increasing L.H.S.V. and decreasing temperature. It was noted that the sulfur was removed from the feedstocks much easier than the nitrogen, even though it was present in a much higher concentration.

The "optimum" catalyst composition was determined by use of a Central Composite Rotatable Design. This catalyst should contain approximately 7 percent nickel (by weight) and 18 percent tungsten (by weight) on the silica-alumina support. It was noted, however, that the response surface was relatively flat over the range of nickel and tungsten contents studied; i.e. , over the nickel content range from 2 to 12 wt.% and tungsten content range from 6 to 26 wt.%.

The results obtained from tests conducted utilizing the nickel promoted tungsten on silica-alumina support catalyst show its superiority to currently available commercially used hydrodenitrogenation catalysts. It is rugged, long-lived, and operates at temperatures and pressures that are moderate and economical to obtain.

TUNGSTEN AS A HYDRODENITROGENATION CATALYST
FOR PETROLEUM OIL FRACTIONS

by

ARTHUR YNGVE FALK

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

of

DOCTOR OF PHILOSOPHY

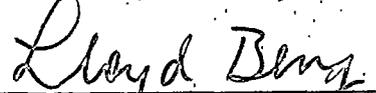
in

Chemical Engineering

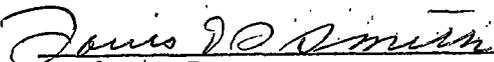
Approved:



Head, Major Department



Chairman, Examining Committee



Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1967

ACKNOWLEDGMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State University, and in particular, Dr. Lloyd Berg who directed this research. The author is indebted to Dr. Lloyd Berg, Dr. Robert L. Nickelson, and Dr. Charles J. Mode for their encouragement, advice, criticism, and assistance which led to the successful completion of this project.

The author also wishes to acknowledge the Engineering Experiment Station of Montana State University for the financial support given this project. The helpful assistance of many petroleum companies and catalyst and/or chemical companies too numerous to mention is also acknowledged with thanks.

To his wife, Ella, a special acknowledgment is due for her patience and understanding during the time that this thesis was being effectuated.

TABLE OF CONTENTS

	Page
List of Tables	vi
List of Figures	vii
Abstract	ix
Introduction	1
Research Objectives	7
Experimental Considerations	8
A. Introduction	8
B. Materials	20
C. Equipment	22
D. Operating Procedures	24
E. Analytical Procedures	28
F. Catalyst Preparation Procedures	30
Experimental Research Plan	33
Discussion and Interpretation of the Experimental Results	37
Introduction	37
Exploratory Tests	38
Preliminary Catalyst Preparation Tests	57
Experimental Design and Catalyst Evaluation Comparison Test Results	70
Summary and Conclusions	88
Recommendations for Further Work	91

TABLE OF CONTENTS (continued)

	Page
Appendix	93
Tables	94-144
Figures	4, 71, 145-164
Literature Consulted	165

LIST OF TABLES

	Page
TABLE I	Comparison of Commercial Catalysts' Hydrodenitrogenation Activity 44
TABLE II	Analysis of Variance Results for Exploratory Tests 48
TABLE III	Experimental Design Test Points 72
TABLE IV	Comparison of the Desired and Actual Metal Contents of the Design's Catalysts 74
TABLE V	Experimental Design Points Test Order 75
TABLE VI	Experimental Design (Analysis of Variance; One-Way Classification with Unequal Replication and Equal Subsample Numbers.) 77
TABLE VII	Experimental Design Conversion Data 79
TABLE VIII	Analysis of Variance: Central Composite Rotatable Design 80
TABLE I-A	Feedstock Properties 94
TABLE II-A	Commercial Catalysts Properties 95
TABLE III-A	Catalyst Support Properties 97
TABLE IV-A	Properties of the Prepared Catalysts 99
TABLE V-A	Tabular Summary of Run Numbers, Operating Conditions, and Run Objective(s) 100
TABLE VI-A	Experimental Nitrogen and Sulfur Conversion Data 113
TABLE VII-A	Catalyst Life Test Feedstock and Product Analyses 143
TABLE VIII-A	Effluent Gas Analyses 144

LIST OF FIGURES

	Page
Figure 1	Typical Nitrogen Compounds Found in Petroleum 4
Figure 2	Experimental Design Layout 71
Figure 1A	Schematic Flow Diagram of the Hydro- treating Unit 145
Figure 2A	Detailed Diagram of the Reactor 146
Figure 3A	Effect of Hours on Stream and Catalyst Pre- sulfiding on Catalyst Hydrodenitrogenation Activity for a Commercial Cobalt Molybdate Hydrotreating Catalyst 147
Figure 4A	Effect of Hydrogen (Hydrotreating) Gas Feed Rate on the Hydrodenitrogenation Activity of the Hydrotreating Catalysts 148
Figure 5A	Experimental Test for Film Diffusion Controlling the Catalysts' Activity 149
Figure 6A	Effect of Liquid Hourly Space Velocity on a Commercial Nickel-Cobalt-Molybdate Hydro- treating Catalyst's Hydrodenitrogenation Activity 150
Figure 7A	Effect of Temperature on a Commercial Nickel- Cobalt-Molybdate Hydrotreating Catalysts's Hydrodenitrogenation Activity 151
Figure 8A	Extended (90 Day) Catalyst-Life Test Results For a Nickel-Tungsten Catalyst 152
Figure 9A	Effect of Feedstock Properties and Temperature on Nickel-Tungsten Catalyst Activity for Hydro- denitrogenation. (Extended Catalyst-Life Test -- Initial Portion.) 153
Figure 10A	"Initial" Preliminary Catalyst Preparation Test Results 154
Figure 11A	Effect of Metal Impregnation Order on the Catalyst's Activity. (Nickel-Tungsten Catalyst.) 155

LIST OF FIGURES (continued)

	Page
Figure 12A	Effect of Catalyst Preparation Repeatability and Test Run Duplication on the Resulting Catalyst's Activity. (Nickel-Tungsten Catalyst.) . . . 156
Figure 13A	Evaluation of Promoters for a Tungsten Type Hydrodenitrogenation Catalyst 157
Figure 14A	Effect of Catalyst Pretreatment Method on Catalyst Hydrodenitrogenation Activity. (Nickel-Tungsten Catalyst.) 158
Figure 15A	Catalyst Support Evaluation (Comparison) for Nickel-Tungsten Hydrodenitrogenation Catalyst 159
Figure 16A	Response Surface for Nickel-Tungsten Catalyst 160
Figure 17A	Catalyst Hydrodenitrogenation Activity Comparison. (Feedstock No. 1) 161
Figure 18A	Catalyst Hydrodenitrogenation Activity Comparison. (Feedstock No. 3) 162
Figure 19A	Effect of Temperature on the Developed Nickel-Tungsten Catalysts' Hydrodenitrogenation and Hydrodesulfurization Activity 163
Figure 20A	Effect of Liquid Hourly Space Velocity on the Developed Nickel-Tungsten Catalysts' Hydrodenitrogenation and Hydrodesulfurization Activity 164

ABSTRACT

The catalytic hydrodenitrogenation of high nitrogen content petroleum gas oils was studied. The primary objective of this research was to discover and/or develop a catalyst which could effectively remove nitrogen from high nitrogen content petroleum gas oils. A catalyst was sought which would be more effective at removing the nitrogen from the gas oil than the present commercially used cobalt/nickel molybdate catalysts.

The study was carried out on a bench scale, continuous, tubular flow reactor. The operating conditions utilized during this study were: temperature 700 to 820°F., pressure 1000 psig, hydrogen flow rate of 5000 SCF/bbl. of oil, space velocity (L.H.S.V.) 0.25 to 2.0 ml. of oil/hour/ml. of catalyst. (In order for the hydrodenitrogenation process to be economically as well as technically sound, the pressure was limited to no greater than 1000 psig.) The primary feedstock source was the Santa Maria (California) crude source. The feedstocks, whose boiling ranges were approximately 550°F to 900°F, contained between 0.181 and 0.335 wt.% nitrogen. All nitrogen conversion calculations were based on the total nitrogen concentrations determined by the Boyd Guthrie modification of the Kjeldahl method.

A nickel-tungsten type catalyst, on a silica-alumina support, more active than the present commercially used cobalt/nickel molybdate hydrodenitrogenation catalysts was developed. Use of a silica-alumina support, containing 5 to 7 percent silica (SiO_2) by weight, was found to result in a more active catalyst than a similar catalyst on an alumina support. Of the conventional hydrotreating catalyst promoters (nickel, cobalt, and molybdenum), nickel was found to be the most effective promoter for the tungsten type hydrotreating catalyst. The catalyst was found to be more effective (active) if properly sulfided prior to use.

As expected, the developed catalysts' activity decreased with increasing L.H.S.V. and decreasing temperature. It was noted that the sulfur was removed from the feedstocks much easier than the nitrogen, even though it was present in a much higher concentration.

The "optimum" catalyst composition was determined by use of a Central Composite Rotatable Design. This catalyst should contain approximately 7 percent nickel (by weight) and 18 percent tungsten (by weight) on the silica-alumina support. It was noted, however, that the response surface was relatively flat over the range of nickel and tungsten contents studied; i.e., over the nickel content range from 2 to 12 wt.% and tungsten content range from 6 to 26 wt.%.

The results obtained from tests conducted utilizing the nickel promoted tungsten on silica-alumina support catalyst show its superiority to currently available commercially used hydrodenitrogenation catalysts. It is rugged, long-lived, and operates at temperatures and pressures that are moderate and economical to obtain.

INTRODUCTION

In recent years the nation's proven reserves of petroleum and its consumption of petroleum products have both been increasing. A major contributor to the increased consumption of petroleum products has been the rapidly expanding petrochemical industry. Although at present the nation's, and the world's, proven reserves of petroleum exceed the demand for it, technologists have become vitally concerned with processes whereby other oils could be used in place of petroleum products. This is evidenced by the Synthetic Liquid Fuels Act passed by the United States Congress in 1944 which authorized research and development of new sources of oil. With this increasing demand from the petrochemical industry and other users of oil, it is felt that a time may arrive in the foreseeable future when the demand for petroleum products will exceed their supply. Therefore, investigations into processes whereby other oil sources could be used as petroleum substitutes have been under way in recent years (4, 13, 14, 40, 42). The main sources of petroleum substitutes appear to be shale-oil, liquid and gaseous products from coal hydrogenation, and the oil from the tar sands in Alberta (Athabasca), Canada.

Keeping the above trends in mind, it should be noted that the nation's supply of crude petroleums that are free from considerable quantities of nitrogen, sulfur, and oxygen-containing compounds (high quality crude sources) are rapidly being depleted. Generally, crude petroleums with greater than approximately 0.1 wt.% nitrogen could be considered to have a high quantity of nitrogen (3). The main sources of petroleum substitutes

all contain considerable quantities of nitrogen-, sulfur-, and oxygen-containing compounds, especially when compared to crude sources that have been used in the past (1, 3, 11). For example, crude shale-oil from the vast beds of oil shale in Colorado contains approximately 2 percent by weight nitrogen (1).

In general, it has been noted that the presence of nitrogen-containing compounds in oil sources are undesirable (12, 16, 22, 24, 27, 30, 34, 41). They have an adverse effect on the petroleum products and the catalysts used in the refining of the oils. Nearly all petroleum processes are catalytic in nature and it has been noted that nitrogen compounds in the feedstock(s) to most of these processes is detrimental to the catalyst (s) used. For example, the much used silica-alumina cracking catalyst is poisoned (deactivated) by nitrogen compounds in the feedstock to the catalytic cracking unit (27, 30). Kiovsky and others have noted the adverse effect of nitrogen compounds in petroleum fractions on the activity of the much used cobalt molybdate hydrodesulfurization catalyst (22, 24). Even one of the most recently developed catalytic petroleum processes, hydrocracking, is adversely affected when nitrogen-containing compounds are present in its feedstock (34). Various sources have noted that insoluble gums and color instability are characteristic of petroleum products which contain nitrogen compounds (12, 37, 41). These products are also noted for their unpleasant odor.

In order to eliminate these undesirable characteristics of oils which contain nitrogen, the nitrogen must be completely removed. Concentra-

tions of even a few parts per million of nitrogen can cause these undesirable characteristics in oils. Although much work has been done toward upgrading these oils, a definite need still exists for a more efficient and/or effective means of removing the nitrogen from the oils. The upgrading, by nitrogen removal, of the petroleum substitute oils and high nitrogen content petroleum oil sources is a challenging problem.

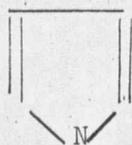
Destructive catalytic hydrogenation seems to be the most selective means of removing the nitrogen from the oils since it removes only the nitrogen atoms from the original compound. Destructive catalytic hydrogenation involves passing the oil stock together with hydrogen over a suitable catalyst at relatively high temperatures and pressures. The net result is that the hydrogen reacts with the nitrogen compound to give a hydrocarbon and ammonia.

The nitrogen compounds in petroleum, shale-oil, and coal products are very similar in nature (11, 15, 26, 28, 35). They are generally heterocyclic, with the nitrogen incorporated in either a five- or six-membered ring. The ring is usually unsaturated. The nitrogen compounds are classified as basic or non-basic. The five-membered ring compounds are frequently non-basic, with hexahydrocarbazole and indoline as notable exceptions, while the six-membered ring compounds are generally unsaturated and basic. This classification is based upon the ability of the nitrogen compound to interact with a perchloric acid-acetic acid solution. Approximately 30 percent of the nitrogen compounds in a typical straight run petroleum stock are basic. The configuration of some of the

typical nitrogen compounds in petroleum or its potential substitutes are shown on the following page. (Homologs and derivatives of quinoline, pyridine, and pyrrole are the most common nitrogen compounds found in petroleum, shale-oil, and coal hydrogenate.)

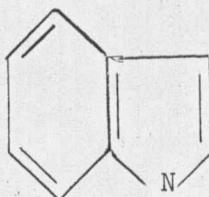
TYPICAL NON-BASIC COMPOUNDS

Pyrroles



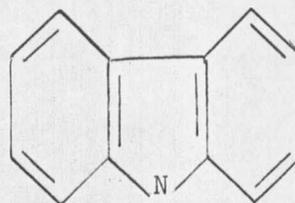
H

Indoles



H

Carbazoles



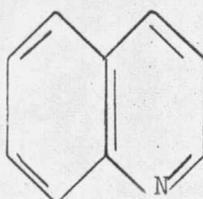
H

TYPICAL BASIC COMPOUNDS

Pyridines



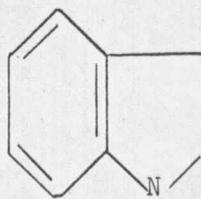
Quinolines



Amines

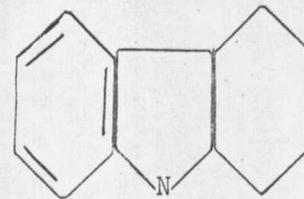


Indolines



H

Hexahydrocarbazoles



H

Figure 1. Typical Nitrogen Compounds Found in Petroleum.

The removal of sulfur from petroleum or petroleum substitutes is no longer a problem. Cobalt molybdate and/or nickel molybdate catalysts, on an alumina support, do an adequate job of removing the sulfur from these oil sources (7). Presently, these catalysts are also used to remove the

nitrogen from petroleum fractions. In general, nitrogen is harder to remove from oils than sulfur and the presently used cobalt and/or nickel molybdate catalysts do not do an adequate job of removing the nitrogen from high nitrogen content oils even at extremely severe operating conditions (7). Also, as noted previously, cobalt molybdate catalysts are adversely affected (deactivated) by the nitrogen compounds in the oils. During the catalytic hydrotreating of oils it has been learned that when the nitrogen comes out, the sulfur does, too (7).

Since the petroleum substitutes mentioned herein all contain a rather high content of nitrogen, and their use is expected to increase shortly, it would seem apparent that some serious effort should be expended to develop a process and/or catalyst for removing the nitrogen from these oils that is more effective than those presently available.

The reactions involved in the hydrogenation of complex mixtures of nitrogen compounds in an oil stock are numerous and complex in nature (15, 36). In previous research at Montana State University, extensive investigations have been conducted in order to gain information on these complex reactions. For example, the destructive catalytic hydrogenation of quinoline was studied extensively by Ryffel and that of pyridine and pyrrole by Schreiber (36, 38). Cox studied the destructive catalytic hydrogenation of some of the derivatives of these compounds (10). The catalytic hydrogenation of shale oil fractions was also investigated in previous work carried out at Montana State University (4).

In light of the facts presented herein, it would seem that there is presently a definite need for a "better" catalyst more active, effective, and durable than the presently used cobalt and/or nickel molybdate catalysts, to remove nitrogen from petroleum fractions. Since the nitrogen in nearly all petroleum process feed streams is undesirable, it would seem most beneficial to remove the nitrogen from the oil source as early in the refinery processing of the oil as possible. It was for this reason that the research work presented herein was conducted. This work was conducted utilizing high nitrogen content petroleum gas oils.

It is believed that the results of this research should be of considerable practical value. Since the nitrogen compounds in petroleum are similar in nature to those in the potential petroleum substitutes, the results of the work presented herein should be applicable to the processing of the potential petroleum substitute oils.

RESEARCH OBJECTIVES

The overall objective of this research work was the process development of the catalytic hydrodenitrogenation of high nitrogen content petroleum gas oils. This hydrodenitrogenation process should be economically as well as technically sound.

The primary objective of this research was to discover and/or develop a catalyst which could effectively remove nitrogen from high nitrogen content petroleum gas oils. A catalyst was sought which would be more effective at removing the nitrogen from gas oil than the present commercially used cobalt/nickel molybdate catalysts. This catalyst should have the capability of high nitrogen removal and long catalyst life. A secondary objective of this research was to obtain information on the effect of process variables on the nitrogen removing capability of the catalyst. In particular, the operating variables of principal interest were space velocity and temperature.

In general, the above objectives were realized insofar as time and available equipment allowed.

EXPERIMENTAL CONSIDERATIONS

A. Introduction

This section of the thesis is intended to present and discuss experimental considerations only to the extent and for the purpose of pointing out the importance of considering the factors presented. The actual experimental methods and techniques used in taking these factors into account will be discussed in the Discussion and Interpretation of the Experimental Results section of the thesis.

Before experimental work was initiated, a review of the literature was conducted in order to determine the experimental variables that should be investigated. The operating conditions, (i.e., the range of the variables that should be used), were selected after the literature review and several exploratory test runs. Consideration was given mainly to keeping the conversion in the 10 to 90 percent range for the catalyst activity comparison tests. This was so that catalyst activity differences could be more easily detected. The limitations of the equipment, analytical techniques, expense, and the time requirements were also considered. This literature review was helpful in acquainting the author with experimental techniques that were of considerable value, and also possible experimental "pitfalls" that should be avoided. The most pertinent results of the pre-experimental literature review are presented below.

In general, it is noted that the high nitrogen content petroleum crude sources are located in the California area (3). The nitrogen content of crude petroleums generally vary between 0 and approximately 0.9 wt.% (3).

Therefore, for the experimental work reported herein, high nitrogen content heavy gas oils from the California area were utilized.

One of the primary objectives of this research work was to develop a catalyst more active than the present commercially available cobalt/nickel molybdate catalysts used for removing nitrogen from petroleum feedstocks. Present catalysts cannot completely remove the nitrogen from high nitrogen content gas oils even under severe operating conditions (7, 15, 20). At present, high temperatures and pressures are needed to obtain even a reasonable degree of denitrogenation of petroleum gas oils (20). At temperatures much above 800°F, substantial cracking of the hydrocarbon oil and coke formation normally occurs, and the production of light gases increases markedly. With a less active catalyst the temperature at the start of the run must be much higher, and the on-stream time between catalyst regenerations is correspondingly reduced. More active catalysts would make possible the use of lower temperatures and be usable for long periods of time. Hence, a special feature of a highly active catalyst is its relatively low operating temperatures and the resultant long catalyst life. A highly active catalyst also has the advantage that it permits the use of higher space velocities in treating hydrocarbon oils.

In view of the fact that experience has shown that operating temperatures much in excess of 800°F are not feasible without excessive coking of the catalyst used, this was selected as the probable maximum temperature to be used in the catalyst comparison test runs. The initial exploratory tests verified that 800°F was a suitable temperature for the catalyst comparison tests.

It is well known that in the hydrotreating of oils the greater the operating pressure the greater is the nitrogen removing capability of the catalyst used. This, of course, assumes that the other variables are held constant. Since we were seeking a hydrodenitrogenation process that was economically as well as technically sound, we limited the operating pressure to not more than 1000 psig. Pressures above 1000 psig are expensive to obtain.

It is noted that in most hydrotreating processes the conversion obtained drops sharply during the first few hours of reactor operation and then levels off to a reasonably constant value thereafter (10, 36, 38). This sharp change in conversion is attributed mainly to the initial adsorption of the oil upon the catalyst until it is completely saturated and equilibrium is established. The slight decrease in conversion, with time, thereafter occurs because of a decrease in catalyst activity caused in the most part by blocking of the active sites on the catalyst due to carbon deposition. Therefore, effort was made to insure that a catalyst's activity was measured after the initial transient conversion period.

When solid catalysts are being employed, as in this work, care should be taken in order to make sure that the catalyst is being used to its fullest capacity. That is, tests should be made to insure that one of the physical diffusion steps is not the "rate controlling step" in the reaction mechanism. If film diffusion is controlling, it means that either the reactant molecules cannot be supplied to the catalyst or that

the product molecules cannot be removed fast enough to keep up with the potential ability of the catalyst to cause the reaction to proceed. This occurs because the reactants and products must diffuse through a stagnant layer of gas/liquid that surrounds the catalyst pellet. Experimental tests were conducted in order to insure that film diffusion was not the "rate controlling step" and that the catalysts were being used to their fullest capacity.

Since for most solid catalysts the outside surface area is negligible in comparison to the inside surface area, care should be taken to insure full use of the interior (inside) surface area of the catalyst. Failure to do this could result in not using the catalyst to its fullest capacity. In order for the interior surface to be used to its fullest capacity, the reactant molecules must diffuse into the catalyst pores and the product molecules must diffuse out of the catalyst pores at a rate fast enough to keep up with the potential ability of the catalyst to cause the reaction to proceed.

Another experimental factor that warrants consideration is the pre-treatment of the catalyst prior to its use for hydrotreating. Experience has indicated that sulfided hydrotreating catalysts, (i.e., catalysts with the metals in the sulfide form), seem to be more active than the corresponding metal oxide catalysts (20, 22). Therefore, the effect on the catalyst's activity of sulfiding it prior to use was investigated.

Space velocities, volume of oil per hour per volume of catalyst, used during the experimental work were selected with two basic (important) criteria in mind. For the most part, consideration was given to keeping the conversion of nitrogen in the 10 to 90 percent range for easy comparison of the catalysts tested. This conversion range is also most desirable when determining the effect of process variables on the nitrogen removing ability of the catalysts. Also, space velocities were utilized that would be feasible for industrial use.

The hydrogen flow rate to the reactor can also be an important experimental factor and should be investigated. Mainly, the hydrogen flow rate should be kept large enough so that it is not limiting the catalyst's ability to remove nitrogen from the oil (activity), especially in a study where different catalysts are being compared, as herein. Of course, the expense should be considered in the selection of the hydrogen flow rate (consumption) since hydrogen is expensive. The hydrogen flow rate used for the work presented here was much larger than stoichiometrically necessary. In fact, no significant difference in nitrogen conversion was noted even at considerably high hydrogen flow rates.

In general, the experimental considerations presented up to now have been applicable to both the commercial catalyst evaluation and catalyst development phases of the work presented here. Now, the results of a literature search which eventually led to the catalyst development effort presented here is put forth and discussed.

The results that may be obtained from a thorough study of a presently used catalyst for a specific purpose are illustrated very well in U.S. Patent No. 3,114,701 (reference 20) issued in December 1963. In this patent the increased denitrogenation ability of nickel molybdate catalysts, on an alumina support, in the range containing 4-10 percent nickel together with 15.5 - 30 percent molybdenum by weight is noted over the conventionally used nickel molybdate hydrotreating catalysts.

Conventional nickel molybdate and cobalt molybdate catalysts usually contain only about 10 to 12 percent by weight (total) of the metals. These conventional catalysts were developed originally for hydrodesulfurization purposes.

A thermodynamic feasibility study, based on an assumed mechanism, of various metals as effective hydrodenitrogenation and hydrodesulfurization catalysts indicated the possibility that tungsten disulfide, along with various other metal compounds, might possibly be an effective hydrodenitrogenation catalyst.

Shell Oil Company has previously used a catalyst, for petroleum hydrotreating purposes, consisting of pellets containing 48 percent tungsten, 20 percent nickel, and 25 percent sulfur (8, 29). The remaining percentage is iron, carbon, and unidentified material. Shell has discontinued use of this tungsten nickel sulfide catalyst. Recently the Harshaw Chemical Company has started to offer commercial nickel, in the reduced form, tungsten sulfide catalysts for hydrocracking and other hydro-

treating purposes. One of these catalysts contains 6 percent nickel and 19 percent tungsten and is available on either an alumina or silica-alumina base. The other, containing 4.5 percent nickel and 9.5 percent tungsten, is available on an alumina base. The silicon dioxide (SiO_2) content of the first catalyst when on the silica-alumina base is approximately 50 percent, by weight. It should be noted that tungsten has been employed for various catalytic processes (25).

In the August 17, 1963 issue of Chemical Week (reference 7) an article titled "Catalysts" contained the following statements about hydro-treating catalysts, in general, and Harshaw's 6 percent nickel, 19 percent tungsten catalyst, mentioned above, in particular. "Originally the big job for hydrotreating catalysts was to remove sulfur. Now, it's to get the nitrogen out. It has been learned that when the nitrogen comes out, the sulfur does, too. Catalysts are cobalt molybdate or nickel molybdate on alumina with or without silica. Harshaw Chemical Company is marketing a catalyst containing 6 percent nickel, 19 percent tungsten on an alumina-silica support as a hydrocracking catalyst."

It should be noted here that a catalyst that effectively removes nitrogen from a refinery stream will also, in general, effectively remove the sulfur from the stream.

U.S. Patent No. 3,114,701 clearly indicates the results that may be obtained by the thorough study of a general hydrotreating catalyst for a specific purpose. In this case, a conventional desulfurization cat-

alyst was studied thoroughly and improved to make it a more active hydrodenitrogenation catalyst. On the basis of this and the other facts presented above, it was decided that a thorough study of tungsten as a hydrodenitrogenation catalyst seemed warranted.

Before setting up the research plan for the development of a tungsten type hydrodenitrogenation catalyst, the literature and U.S. Patents were reviewed for helpful information in deciding upon the best research plan. The results of this review of available material, which was very fruitful, are presented below.

Since catalyst preparation and manufacture is sometimes considered to be more of an art than a science, it is felt that the initial step in any catalyst development program should be the verification of the ability to prepare an active catalyst of the type desired, in the laboratory (18). Experimental verification of the repeatability of the catalyst's preparation and activity should also be determined early in the development program.

A third factor that should be studied is catalyst pretreatment. This factor should be examined because although most people claim hydrotreating catalysts should be sulfided to increase their activity, the temperature of sulfiding and the degree (amount) of sulfiding are controversial issues. Most people claim hydrotreating catalysts should be sulfided at 600-700°F (20); others claim more active catalysts are obtained by sulfiding between 110-210°C (31). The important thing to note is that

both the sulfiding temperature and the amount of sulfur passed over the catalyst could possibly influence its activity. Many sulfur sources have been used in the sulfiding of catalysts. In general, little difference in catalyst activity has been noted due to the source of sulfur used for sulfiding (20, 22, 31, 43, 44). One of the most effective and simple means seems to be to utilize a gaseous hydrogen-hydrogen sulfide mixture.

Since most hydrotreating catalysts contain more than one metal, the possibility of promoting a tungsten catalyst with one of the conventional hydrotreating catalyst promoters should be examined.

Two other factors that it is essential to investigate are the order of metal impregnation on the catalyst support and the catalyst support used. Both of these factors can have a significant influence upon the catalyst's activity, as noted in U.S. Patent No. 3,114,701 and U.S. Patent No. 2,744,052. Other literature sources and personal correspondence with catalyst manufacturers have also pointed out the importance of using the proper carrier. The proper carrier can greatly enhance a catalyst's activity. The method of catalyst preparation can also greatly affect its activity (5, 18).

Literature sources using various supports for hydrotreating catalysts indicate that alumina and alumina-silica supports are generally the most adequate supports. Such supports as TiO_2 , MgO , and SiO_2 for hydrotreating catalysts generally do not work very well in comparison to the alumina or alumina-silica supports (31). Therefore, for this research

work, only alumina and alumina-silica type supports were evaluated.

That alumina-silica supports will probably yield catalysts of higher activity than corresponding alumina supports is noted in the literature (31). This is because of the cracking property of the alumina-silica. If the silica content is less than 6 percent, the undesirable cracking activity is usually not present. (Excessive cracking is undesirable since it causes carbon deposition on the catalyst which results in catalyst deactivation). In fact, according to U.S. Patent No. 2,437,532 the presence of small amounts of silica can serve to stabilize the resulting catalyst and prolong the catalyst life (19). For this work the silica content in the silica-alumina supports was kept below the 6 percent level.

In review, the objectives that are felt essential to accomplish in preliminary catalyst preparation test runs are:

- (1) To determine if it is possible to prepare an active catalyst, of the type mentioned above, in the laboratory.
- (2) To determine if the preparation of such a catalyst is reasonably repeatable.
- (3) To determine the effect that sulfiding temperature and the amount of 80 percent hydrogen-20 percent hydrogen sulfide (by volume) mixture that is passed over the catalyst has on its activity. (Other pretreatment techniques were also tried.)

- (4) To determine the effect of nickel, cobalt, and molybdenum on the tungsten catalyst as promoters.
- (5) To determine if the order of impregnation of the metals affects the catalyst's activity.
- (6) To determine if the catalyst's support has an important effect on the catalyst's activity. (That is, various supports were evaluated and the best one chosen.)

After the above six objectives were accomplished, an experimental design was carried out using the best catalyst support, proper catalyst pretreatment, and the best promoter for the tungsten. The purpose of this design was to determine the optimum weight percent of each metal that should be impregnated on the support to give a catalyst of maximum denitrogenation activity. (This design is discussed in detail in the Discussion and Interpretation of the Experimental Results section of the thesis.)

With due consideration for the information presented above, which was obtained from a literature review and a few exploratory tests, the following operating conditions were chosen.

- (1) A reactor pressure of 1000 psig was utilized for all tests.
- (2) Space velocities between 0.25 and 2.0 ml of oil per hour per ml of catalyst were utilized for most tests. (A few tests were conducted at higher space velocities.) The majority of the catalyst comparison tests were conducted

at a space velocity of 0.5.

- (3) Temperatures between 700-800°F were utilized with the exception of a few tests. The majority of the catalyst comparison tests were conducted at 800°F.
- (4) For all tests except those to investigate the effect of hydrogen flow rate on the nitrogen conversion, a hydrogen flow rate of 5000 standard cubic feet of hydrogen per barrel of oil was employed. This hydrogen flow rate is much larger than is stoichiometrically necessary. No significant difference in nitrogen conversion is noted even at higher hydrogen flow rates.
- (5) The feedstocks were heavy gas oils from the California area. These gas oils contained between approximately 1800 and 3400 parts per million nitrogen.
- (6) The catalyst charge to the reactor was varied from 30 to 120 ml, depending on the space velocity being employed. Most tests utilized a 120 ml catalyst charge. The support usually consisted of either 1/8-inch pellets or extrusions.

In most catalyst development studies it is practically essential, if at all feasible, to conduct a catalyst life test. This project was not an exception. Therefore, a catalyst life study was conducted with a nickel tungsten sulfide catalyst.

B. Materials

The feedstocks used for this research work were all high nitrogen content petroleum gas oils. All feedstocks were obtained from California crude sources which are noted for their high nitrogen content (3). The weight percent nitrogen in the gas oils varied from 0.181 to 0.335 (1810 to 3350 ppm). Table I-A, page 94, lists the pertinent properties of the oils that were treated. The California Research Corporation at Richmond, California provided the major portion of the gas oil used for this research project. These gas oils were from the Santa Maria (California) area and their boiling range was approximately 550°F to 900°F.

Table II-A, page 95, lists the commercial catalysts that were tested during this project along with their pertinent properties. Essentially all of the catalysts were in the form of 1/8-inch by 1/8-inch pellets or extrusions. All of the cobalt/nickel molybdate hydrotreating catalysts listed in Table II-A are commercially available. All are on an alumina support.

The inert catalyst support materials used in the pre-heat and after-heat sections of the reactor were either 1/4-inch or 1/8-inch low surface area alundum pellets. They were obtained from the Norton Company. The 1/8-inch by 1/8-inch alundum pellets were also used, when necessary, to dilute the catalyst charge to occupy a volume of about 120 ml in the center of the reactor. (This constituted the catalyst zone of the reactor.)

Table III-A, page 97, lists the various alumina and silica-alumina supports considered for use in the catalyst preparation phase of this research project. (The actual supports tested are also noted.) The reasons for selecting the supports that were tested is discussed in the Discussion and Interpretation of the Experimental Results sections of this thesis. The supports tested were all in the form of 1/8-inch by 1/8-inch pellets or extrusions.

Commercially available, chemically pure, chemicals were utilized for the preparation of all catalysts. Cobalt nitrate, nickel nitrate, ammonium molybdate, tungstic acid, and aqueous ammonia were employed in the preparation of the catalysts. Most of these chemicals were obtained from the Fisher Chemical Company.

The pure hydrogen treat gas employed was supplied in high pressure cylinders by H-R Oxygen and Supply of Billings, Montana. The hydrogen gas was passed through a "Deoxo" unit to remove trace quantities of oxygen before being used. The hydrogen-hydrogen sulfide gas mixture was obtained from the Matheson Company of Joliet, Illinois. It was a 20 percent hydrogen sulfide-80 percent hydrogen mixture (by volume). This mixture was used in the sulfiding (pretreatment) of nearly all the catalysts tested.

Other materials that were employed were cyclohexane, carbon disulfide, pyridine, and Penetec. These materials were used for catalyst pretreatment studies, as will be noted later.

C. Equipment

A schematic flow diagram of the catalytic hydrotreating unit is shown in Figure 1A, page 145. The reactor is operated as a fixed bed, continuous-flow, integral reactor. A detailed diagram of the reactor is shown in Figure 2A on page 146.

The feedstock, a high nitrogen content petroleum gas oil, is pumped from its reservoir to the top of the reactor where it enters with the hydrogen. The hydrogen which is metered from the hydrogen cylinder has been deoxygenated, dried, and filtered. The "Deoxo" unit contains a palladium catalyst which removes the oxygen by catalytically combining it with hydrogen to form water. The water is then removed by passing the stream through a tube packed with a material suitable to absorb the water. The feed and hydrogen then pass down through the pre-heat, catalyst, and after-heat zones of the reactor, (Figure 2A). The reaction mixture consists of gaseous hydrogen and the feedstock which is partly vapor and partly liquid as it passes through the catalyst zone of the reactor. After passing through the reactor, the resultant products are cooled and condensed under pressure in a countercurrent water condenser. After passing through a back-pressure regulator, the reactor products are passed through another condenser which consists of a cooling coil immersed in an ice bath. This is to insure complete recovery of the condensable vapor products. The liquid product is collected in a flask while the gaseous products are scrubbed before being vented to the atmosphere (Figure 1A).

The reactor was made from a 1-inch (outside diameter), schedule 80 seamless type 18-8 stainless steel pipe approximately 30 inches in length. Flanged unions were welded to both ends of the reactor. The top flange was permanently joined to a high pressure cross containing a 1500 psia rupture disc in one of the side arms. This rupture disc was inserted as a safety device. A thermowell entered the reactor through the top of the cross, and the feedstock and hydrogen mixture through the other side-arm of the cross. The flange at the bottom of the reactor was such that it permitted easy access to the inside of the reactor.

The reactor was covered with a layer of asbestos tape and then wrapped with five ceramic-beaded nichrome heating coils (Figure 2A). The heating coils were covered with approximately two inches of a magnesia type insulation. The heating coils were connected to 110-volt, constant voltage Powerstats which were used to regulate the current supply to the coils.

A length of 3/16-inch (outside diameter) stainless steel tubing, brazed shut at the lower end, extended through the middle of the reactor and served as the thermowell. It extended to within approximately one inch of the bottom flange. Four iron-constantan thermocouples were inserted in the thermowell at various positions in the reactor to measure the temperature. The locations of the heating coils, thermocouples, and catalyst bed are shown in Figure 2A. The thermocouples were connected to a Leeds & Northrup indicating potentiometer which read directly in degrees.

Accessory equipment which was also used in the hydrotreating unit is as follows: A Hills-McCanna high pressure proportioning pump; a Brooks armored high pressure rotometer; a Grove (Mitey-Mite) back pressure regulator; 110-volt Powerstats; a 1000 ml glass feed reservoir with attached 50-ml burette side arm for measuring volumetric flow; three Marshalltown pressure gages; a Baker Deoxo Purifier; a Matheson hydrogen regulator; a Matheson hydrogen-hydrogen sulfide regulator. Schedule 80 black-iron piping and Type 304 stainless steel tubing, 1/8-inch outside diameter, were used throughout. Various Hoke valves were used on the unit, as required. Rubber tubing and glass flasks were utilized for collecting the liquid product and scrubbing and venting of the effluent gases.

D. Operating Procedures

Reactor Preparation: Before each test run, the reactor, condensers, Mitey-Mite back pressure regulator, and connecting tubing (Figure 1A) were washed with acetone. After the equipment was dried of the acetone, the reactor (Figure 2A) was inverted on a special stand and filled with the catalyst and alundum pellets in the manner desired. Care was taken to insure that the thermowell was located in the center of the reactor.

The top section of the reactor was filled to within three inches of the catalyst zone with 1/4-inch by 1/4-inch alundum pellets. A three-inch long section of the reactor immediately above the catalyst bed was filled with 1/8-inch by 1/8-inch alundum pellets. These sections above the catalyst bed constituted the pre-heat zone. The three-inch long section of 1/8-inch pellets above the catalyst zone was to insure proper

distribution of the liquid portion of the feedstock over the catalyst and prevent "channeling" of the liquid down the wall of the reactor. In the 1-inch outside diameter reactor, channeling of the liquid feed could possibly occur in the reactor if 1/4-inch pellets were used throughout the pre-heat zone.

The new catalyst, diluted to 120 ml with the inert 1/8-inch alundum pellets when necessary, was then added to the reactor. This constituted the reaction zone.

The after-heat zone of the reactor contains a 2-inch long section, next to the catalyst zone, of 1/8-inch alundum pellets. The remainder of the after-heat zone was filled with 1/4-inch alundum pellets to just below the flange. A stainless steel screen, followed by a stainless steel ring to hold the screen in place, was then inserted into the bottom of the reactor to keep the reactor charge in place. The reactor was tapped gently during filling to insure proper (uniform) settling of the catalyst and support materials.

The reactor was then installed into its position in the system (Figure 1A). The feed line, thermocouple leads, vent line, and Powerstat cords were then hooked onto the reactor unit. The entire system was then pressurized and checked for leaks. If no leaks were found, the unit was ready for a test run.

Reactor Operation: In all cases, except as will be noted in the Discussion and Interpretation of the Experimental Results section of this

thesis, the catalyst was presulfided in the reactor to convert the metals from the oxide to the sulfide form. Nickel oxide (NiO) and/or cobalt oxide (CoO) together with molybdenum oxide (MoO₃) catalysts, on alumina supports, are more active for hydrotreating purposes when they are sulfided prior to use. This was also found to be the case for the nickel oxide (NiO) - tungsten oxide (WO₃) type catalysts, on alumina/silica-alumina supports developed during this research project. Generally, the catalyst was presulfided with a 20 percent hydrogen sulfide -- 80 percent hydrogen mixture (by volume) at 650°F prior to use. Sulfur equal to approximately 1/2 the weight of the catalyst charge was passed over the catalyst during sulfiding at a rate of two standard cubic feet (of gaseous mixture) per hour. This method of sulfiding the catalysts was found to be as effective as any of the methods of sulfiding that were investigated. The exact nature of the other catalyst pretreatment methods that were tested will be discussed later. In general, the reactor was allowed to cool to room temperature before starting the experimental run. But no significant difference was noted between runs started with the catalyst hot (650°F) and those started with the catalyst at room temperature.

It should be noted that most catalyst manufacturers do not recommend that initial contact of an oil feedstock should be made with a hydrotreating catalyst while it is at elevated temperature, (above 200°F). It is felt that initial contact of the catalyst, while hot, with the oil may initiate cracking and cause carbon deposition on the catalyst which

could adversely affect the catalyst's activity.

To start a run, the feed pump was started, the reactor was pressurized with hydrogen to the desired pressure, and the Powerstats were turned on to heat up the reactor. Then the hydrogen flow rate, which was metered by a calibrated rotameter and needle valve, was adjusted to the desired value and the feed pump was set to pump at the desired volumetric flow rate. The Powerstats were then adjusted to yield the desired temperature. The temperature was controlled by manually controlling the Powerstats' outputs. Except during reactor "line out", at the start of the test run, or at night when the reactor was left unattended for 6 to 8 hours, temperatures were checked and recorded every half hour and adjustments were made to the corresponding Powerstats when necessary, to maintain the desired temperature. After reactor "line out" which usually took less than 4 hours, the reactor temperature at all locations (Figure 2A) could be kept very nearly constant and equal without excessive manual adjustment of the Powerstats.

As mentioned previously, effort was made to insure that the catalyst's activity was measured after the initial transient conversion period. Experimental tests indicated that approximately 12 hours of reactor operation were required before the transient conversion period had elapsed. Also, it was noted that the reactor should be allowed to operate at a constant operating condition for several hours, depending on the feed flow rate, before a product sample is taken. This was to insure that a "true" (representative) product sample was obtained.

Consequently, for each test run samples were taken after approximately 8 hours of operation at approximately 4-hour intervals until the test was terminated. This was to insure that the reactor operation had been allowed to "line out" and that the transient conversion period had passed. Each sample was approximately 15 to 50 ml and was collected in a clean 500 ml flask. Most tests were between 24 and 48 hours in duration.

E. Analytical Procedures

The total weight percent nitrogen in the feedstock and product samples was determined by the Boyd Guthrie modification (2) of the Kjeldahl method (11, 23). This method is designed specifically for the determination of total nitrogen in oil fractions. In most cases the determination of the nitrogen content in each sample was run in duplicate. The percent conversion was calculated using the results of the nitrogen content determinations of the feedstock and product samples. Water washing of the samples to remove free nitrogen and then drying them with calcium chloride was shown to be unnecessary in early test runs and was not employed in general. Dilute acid washing of the feedstock or product samples was shown to remove some nitrogen from the samples, as expected. But dilute acid washing of the samples was not employed in most cases.

For those feedstock and product samples on which a sulfur determination was run, the weight percent sulfur was determined by the quartz tube combustion method. A description of this method is contained in

Vol. 24, page 710 of the April 1952 issue of Analytical Chemistry. All of the samples were washed in a dilute caustic solution to remove free hydrogen sulfide and then water washed and dried before being analyzed. The percent sulfur conversion was calculated in a manner similar to that for the nitrogen conversion.

The method of determining the weight percent nickel, cobalt, or molybdenum in the prepared catalysts is discussed below. Only the method used to determine the weight percent nickel will be discussed in detail herein. The other promoters were both used only once each and the basic method used to determine the weight percent of promoter was similar for each promoter. Nickel impregnating solution of known nickel concentration and density were used at all times. The amount of solution that was absorbed by the support (catalyst) was used to estimate the nickel content of the resulting catalyst assuming that the dried and calcined support (catalyst) would contain nickel as NiO. Nickel nitrate impregnating solutions were employed. The nickel content was also calculated from the increase in weight of the catalyst after impregnation, drying, and calcining of the catalyst support, assuming the increase in weight to be NiO. For all practical purposes the resulting nickel content of the catalyst determined by the two methods was identical. The basis for assuming that the nickel is in the form of NiO is noted in references 21 and 33. Personal correspondence with catalyst authorities also validated this assumption. Therefore, the weight percent of promoter on the catalyst was determined from the increase in catalyst weight upon

impregnation and calcining and the known form of the promoter upon the catalyst support:

From personal correspondence with tungsten catalyst manufacturers and K. Nozaki of the Shell Development Company at Emeryville, California the form of tungsten on the tungsten type catalysts, before sulfiding, was established. When impregnated on a silica-alumina or alumina support, from a cold solution made by dissolving tungstic acid in aqueous ammonia, and calcined in the manner described herein, the tungsten is in the form of WO_3 . From the weight gain, upon impregnation and calcining, of the catalyst support and the known form of the tungsten on the support, the tungsten content of the catalysts was determined.

Although in general no detailed analysis of the hydrotreated product was made other than for nitrogen and sulfur removal, a feedstock and product ASTM distillation comparison was conducted on one test. Also several effluent gas samples were analyzed to determine the effluent gas composition. These analyses were conducted by commercial laboratories and will be discussed in detail later.

F. Catalyst Preparation Procedures

The basic method of catalyst preparation used in preparing the catalysts for this research work is presented here. Any variation in the method of catalyst preparation from that given below will be explained in the Discussion and Interpretation of the Experimental Results section of this thesis. The catalyst preparation procedure was varied only for

the purpose of determining the "best method" of preparing the catalyst. The "best method" of catalyst preparation is that method which yielded a catalyst of maximum activity.

In general, the catalysts prepared for use in the research work reported herein were prepared using high surface area 1/8-inch pellets or extrusions of alumina or silica-alumina. All of the supports used are commercially available and were obtained from the manufacturer as noted in Table III-A on page 97.

Prior to impregnation of the support material with the primary metal component, tungsten, the support material was calcined at 900°F for from 12 to 24 hours to remove any absorbed moisture. This has also been noted to increase the resulting catalyst activity in some cases (31). The tungsten was then impregnated onto a known weight of support material from a cold solution made by dissolving 63.5 grams of tungstic acid in 300 ml of 14 percent aqueous ammonia. The impregnated pellets were then dried for 12 hours at 400°F and then calcined at 900°F for from 12 to 24 hours to convert the tungsten to its oxide form (WO_3). The increase in weight of the support material, which now contains tungsten trioxide, was used to determine the percent (by weight) of tungsten in the catalyst. If necessary, similar impregnations of the support with the desired tungsten solution concentration were carried out to obtain a catalyst with the desired tungsten content. After the support with the desired tungsten content was obtained, it was then impregnated with the desired promoter.

The desired promoter was impregnated onto the pellets from a solution of known promoter concentration. Nickel was impregnated onto the pellets from a nickel nitrate solution. Cobalt was impregnated from a cobalt nitrate solution and molybdenum from an ammonium molybdate solution. The promoter was converted to the oxide form by drying and calcining in a manner similar to that used for the tungsten. The promoter content (weight percent) in the catalyst was determined from the increase in weight of the pellets. This was possible because the form of the promoter oxide on the catalyst was known. The promoter content could also have been determined from the amount of known concentration promoter solution absorbed by the pellets.

Between the steps in the catalyst preparation procedure the pellets were kept in a desiccator to insure that moisture was not absorbed by the pellets.

As noted previously, the "prepared" catalysts were sulfided prior to use, in general. Usually this was accomplished by passing a 20 percent hydrogen sulfide-80 percent hydrogen mixture (by volume) of gas over the catalyst at a rate of 2 standard cubic feet (of gaseous mixture) per hour, at 650°F, until sulfur equal to 1/2 of the weight of the catalyst was passed over the catalyst.

Table IV-A, page 99, presents the properties of the prepared catalysts.

EXPERIMENTAL RESEARCH PLAN

In order to accomplish the research objectives set forth for this project the experimental research plan described below was followed. In constructing this plan, prime consideration was given to the information presented in the Experimental Considerations section of this thesis.

First, a few exploratory tests were conducted utilizing a commercially available hydrotreating catalyst in order to determine the following pertinent information:

- (1) The run length necessary to insure complete "lineout" of the catalyst's activity. The conversion drops sharply during the first few hours of operation and then levels off to a reasonably constant value thereafter.
- (2) A reasonable operating temperature range for a study of the effect of temperature on the catalyst's hydrodenitrogenation activity, and the operating temperature to be used in the catalyst activity comparison tests. Prime consideration was given to keeping the nitrogen conversion in the 10 to 90 percent range.
- (3) A reasonable space velocity (volume of oil per hour per volume of catalyst) range for a study of the effect of space velocity on the catalyst's activity, and the space velocity to be used in the catalyst activity comparison tests. Again, prime consideration was given to

keeping the nitrogen conversion in the 10 to 90 percent range.

- (4) The hydrogen flow rate necessary to assure that the hydrogen flow rate does not limit the nitrogen removing ability (activity) of the catalysts. Tests were also conducted to insure that film diffusion was not controlling the reaction rate and thereby the nitrogen conversion.
- (5) The effect that sulfiding of the catalyst has on its hydrodenitrogenation activity. Standard recommended sulfiding procedures were employed as specified by the manufacturer.

Then, several commercially available cobalt/nickel molybdate catalysts which are presently used for hydrotreating petroleum fractions were evaluated to determine their nitrogen removing capability when used to hydro-treat a high nitrogen content petroleum gas oil. This was necessary in order that these catalysts could be compared with the catalyst(s) developed during the work reported herein. The effect of space velocity and temperature on the nitrogen removing capability of these cobalt/nickel molybdate catalysts were also determined. While this work was being carried out; the results of these tests, the literature and thermodynamic calculations, were studied and reviewed in an attempt to uncover a potential hydrotreating catalyst.

After a potential catalyst material (tungsten) was deemed worthy of study as a hydrodenitrogenation catalyst, the following comprehensive catalyst development effort was initiated in order to evaluate and develop the potential catalyst material. Initially, preliminary catalyst preparation tests were conducted with the following objectives:

- (1) To determine if it is possible to prepare an active catalyst, of the type desired, in the laboratory.
- (2) To determine if the preparation of such a catalyst is reasonably repeatable.
- (3) To determine if the order of metal impregnation affects the catalyst's activity.
- (4) To determine the effect of nickel, cobalt, and molybdenum on the tungsten catalyst as promoters.
- (5) To determine the effect that sulfiding temperature and the amount of 80 percent hydrogen - 20 percent hydrogen sulfide (by volume) mixture that is passed over the catalyst has on its activity. (Other pretreatment techniques were also tried.)
- (6) To determine if the catalysts' support has an important effect on the catalyst's activity. That is, various supports were evaluated and the most suitable one chosen.

Utilizing tungsten along with its best promotor, nickel, and the most suitable catalyst support, an experimental design was carried out to deter-

mine the optimum weight percent of each metal that should be impregnated onto the support to yield a catalyst of maximum hydrodenitrogenation activity. The catalysts for this experimental design were prepared and pretreated in the most desirable manner as determined in the preliminary catalyst preparation test runs.

An extended test run, 90 days in length, was conducted to demonstrate the catalyst life capability of the tungsten type catalyst for hydrodenitrogenation. Also, the effects of the process variables, space velocity and temperature, on the nitrogen and sulfur removing capability of the developed catalyst were studied. Of course, the nitrogen removing capability of the developed catalyst was compared with commercially available catalysts presently used for hydrodenitrogenation.

DISCUSSION AND INTERPRETATION OF THE EXPERIMENTAL RESULTS

Introduction:

With the research objectives (page 7) and experimental considerations (pages 8 through 32) in mind, the research plan presented on pages 33 through 36 was constructed. The experimental results obtained by following this research plan are presented and discussed in detail on the following pages.

Table V-A presents a tabular summary, in chronological order, of each test's operating conditions and a brief description of each test's objective(s). Table VI-A presents the experimental nitrogen and sulfur conversion data from these tests. Figures 3-A through 20-A present the experimental data in graphical form and are discussed in detail on the following pages.

The experimental work was divided into three main areas of effort and the results will be presented and discussed here under three separate headings. The main areas of effort were:

- (1) Exploratory Tests
- (2) Preliminary Catalyst Preparation Tests
- (3) Experimental Design and Catalyst Evaluation
Comparison Tests

These main areas of effort are described briefly below. The exploratory tests were utilized to determine pertinent hydrotreating unit operating conditions and procedures and for the evaluation of commercially available

hydrotreating catalysts. Preliminary catalyst preparation tests were conducted in order to evaluate and determine proper catalyst preparation and/or pretreatment methods for the preparation of an "active" hydrotreating catalyst. The experimental design tests were utilized to determine the optimum weight percent of each metal, primary metal and promoter, that should be impregnated onto the support to yield a catalyst of maximum hydrodenitrogenation activity. The effect of the process variables temperature and L.H.S.V. on the developed catalysts's activity were studied. The developed catalyst's activity was also compared with commercially available hydrotreating catalysts.

The feedstocks used for this research work were all high nitrogen content petroleum gas oils. All feedstocks were obtained from California crude sources which are noted for their high nitrogen content. The primary source of the feedstock was from Santa Maria (California) crude oils.

EXPLORATORY TESTS

Preliminary Investigations:

Figure 3-A presents the results of some initial tests conducted utilizing a commercially available cobalt molybdate (Houdry "C") hydrotreating catalyst. As noted in this Figure, the run length necessary to insure complete lineout of the catalyst's activity is approximately twelve hours for both the presulfided and non-presulfided catalyst.

The reason for the decrease in the catalyst's activity during the initial few hours of reactor operation for the presulfided catalysts was dis-

cussed in detail on page 10. For the non-presulfided catalyst, the initial transient catalyst activity period, while apparently of the same duration as for the presulfided catalyst, exhibits a markedly different trend. During the initial transient conversion period the catalyst's activity increases instead of decreases for the non-presulfided catalyst. This increase in the catalyst's activity during the initial hours of the test run is attributed to a partial sulfiding of the catalyst by the sulfur in the feedstock. This sulfur is converted to H_2S gas in the hydrotreating unit. This same phenomenon, partial catalyst sulfiding, was noted by Kiovisky (22) when utilizing a non-presulfided cobalt molybdate (Houdry "C") catalyst for hydrodesulfurization studies.

The results of these initial tests also indicate that an increase in the resulting "lineout" catalyst's activity, for hydrodenitrogenation, results from presulfiding the catalyst, at least for commercially available cobalt molybdate hydrotreating catalysts. This increase in cobalt/nickel molybdate hydrotreating catalyst's activity, when presulfided, was expected since catalyst presulfiding is recommended for maximum catalyst activity by most manufacturers of these types of catalysts when they are to be used for hydrotreating petroleum fractions. In this case (Figure 3-A) an increase of approximately six percent in the nitrogen conversion capability of the catalyst was obtained by presulfiding the catalyst.

Also indicated in this Figure (Figure 3-A) is the high degree of repeatability of a catalyst activity test run.

Standard recommended sulfiding procedures were employed as specified by the catalyst manufacturer. The details of the sulfiding procedure are given on page 100. For all subsequent tests utilizing commercial hydro-treating cobalt/nickel molybdate catalysts, the catalyst was presulfided for maximum catalyst activity. The mean conversion for each catalyst was determined, as noted on page 113, by taking the mean of the conversion for the samples taken after twelve hours on stream. This is the mean of the catalyst's conversion after "lineout".

All tests conducted during this research work were conducted at a reactor pressure of 1000 psig. It is well known that the greater the reactor operating pressure, the greater is the percent nitrogen removed in the hydrotreating process (4, 15, 36). This, of course, assumes that the other variables are held constant. Pressures above 1000 psig are expensive to obtain. Since we were seeking a hydrodenitrogenation process that was economically as well as technically sound, we limited the pressure to not more than 1000 psig. The operating temperature of 800°F was selected as the maximum temperature that would be used in any catalyst activity comparison tests since this is about the maximum temperature that can be used without excessive coking of the catalysts used (4, 20).

The L.H.S.V. of 0.5 was originally used because it is near the minimum value that would be feasible for commercial use and it was felt that a low L.H.S.V. would be required for a reasonable degree of nitrogen removal from the high nitrogen content petroleum gas oils. Subsequent testing proved this to be true.

When solid catalysts are being used, as herein, care should be taken to insure that the catalyst is being used to its fullest capacity. That is, tests should be conducted to insure that one of the physical diffusion steps is not the "rate controlling step" in the reaction mechanism.

Utilizing the above mentioned extreme operating temperature, pressure, and liquid hourly space velocities of 0.50 and 1.0 ml of oil per hour per ml of catalyst, tests were conducted to insure that external film diffusion was not controlling the reaction process and thereby the nitrogen conversion ability of the catalysts. These were the most severe operating conditions except for two tests conducted late in the research effort at a L.H.S.V. of 0.25 and part of a catalyst life test conducted at 820°F. If film diffusion controls the reaction process it would be most significant at the most severe operating conditions.

In order to test for external film diffusion effects, tests were conducted utilizing Houdry "C" catalyst in which the L.H.S.V. and catalyst charge were held constant along with all other operating variables except the H₂ flow rate. The H₂ flow rate was varied from 1,000 to 16,000 SCF/bbl of oil. If film diffusion is rate controlling, the conversion should increase with increasing H₂ flow rate. As noted in Figure 4-A, the results of these tests indicate that for H₂ flow rates in the 5,000 to 15,000 SCF/bbl of oil range, the Houdry "C" catalyst's activity is essentially independent of the H₂ flow rate. Therefore, it was decided that an H₂ flow rate of 5,000 SCF/bbl would be used on future tests to insure that film

diffusion did not limit the catalyst's activity. Higher H_2 flow rates were not utilized because of the expense that would be incurred in the excessive H_2 consumption. As will be shown later, the difference in conversion between the tests conducted at 5,000 and 16,000 SCF H_2 /bbl of oil was within the test procedure experimental error.

The results of the tests conducted utilizing Houdry "C" catalyst indicate that if a much more active catalyst were employed, that possibly the 5,000 SCF/bbl H_2 flow rate might limit the catalyst's activity. But this Figure (Figure 4-A) also shows the results of tests conducted utilizing the most active catalyst tested, the developed nickel-tungsten type catalyst. Again, the results of these tests indicate that an H_2 flow rate of 5,000 SCF/bbl of oil insures that the catalyst activity is not controlled by external film diffusion. All of the other tests conducted during this research work were conducted using an H_2 flow rate of 5,000 SCF/bbl, and it is felt that this H_2 flow rate should have been sufficient to insure that none of the tested catalyst activities were controlled by external film diffusion during any of the tests.

Figure 5-A shows the results of further tests that were conducted to insure that film diffusion was not controlling the reaction process and thereby the nitrogen conversion. Tests were conducted utilizing Houdry "C" catalyst in which the effects of external film diffusion were checked for by making a series of runs at constant L.H.S.V. by different linear velocities. This was accomplished by varying the oil feed rate and volume of catalyst (ml) simultaneously to give the same L.H.S.V. The feed rate was

varied from 30 to 60 ml/hr and the amount of catalyst from 60 to 120 ml for the 0.5 L.H.S.V. tests. For the 1.0 L.H.S.V. tests, the feed rate was varied from 30 ml/hr to 120 ml/hr and the catalyst charge from 30 to 120 ml. If the conversion for the different linear velocities coincide, at the same L.H.S.V., the effect of external film diffusion is negligible; conversely, there is a diffusional effect if the conversions are significantly different for the same L.H.S.V. If film diffusion is rate controlling, an increase in conversion with increasing linear velocity or catalyst charge should be evident. The results of these tests (Figure 5A) indicate that film diffusion is definitely not rate controlling if 60 or more ml of catalyst are used in conjunction with L.H.S.V. of 0.5 or greater. All future tests utilized 120 ml of catalyst except those conducted at a L.H.S.V. of 5.0 utilizing the FG 500-8 catalyst. Therefore, on the basis of the above results it is felt that external film diffusion did not significantly affect the activity of any of the catalysts tested.

Commercial Catalyst Evaluation Tests

At this point in the research work various commercially available hydrotreating catalysts were evaluated. Table II-A lists the properties of these catalysts. The purpose of this part of the research was to gain information on the activity of commercial hydrotreating catalysts as hydrodenitrogenation catalysts. As noted previously, this was necessary so that the developed catalyst could be compared with the catalysts that are used at present for hydrodenitrogenation. Accordingly, a series of

tests were carried out on nine commercially available hydrotreating catalysts and the results are presented in Table I, below. This represents most of the commercially available cobalt/nickel molybdate hydrotreating catalysts that are presently available.

TABLE I. COMPARISON OF COMMERCIAL CATALYSTS' HYDRODENITROGENATION ACTIVITY.

Catalyst and Manufacturer	Wt. % CoO or Co	Wt. % NiO or Ni	Wt. % MoO ₃ or Mo	% N ₂ Removed	
				@ 750°F	@ 800°F
Houdry (Series "C")	3.0; CoO	----	15.0; MoO ₃	66.5	85.0
Davison (Nicomo 12)	1.9; Co	0.3; Ni	10.0; Mo	66.4	----
Cyanamid (HDS-3)	----	3.1; NiO	15.0; MoO ₃	66.6	84.5
Cyanamid (HDS-2)	3.0; CoO	----	15.0; MoO ₃	55.0	----
Girdler (G-35 B)	3.5; CoO	----	10.0; MoO ₃	55.0	----
Filtrol (500-8)	1.25; Co	2.25; Ni	11.0; Mo	46.2	67.7
Filtrol (475-8)	2.8; CoO	----	15.0; MoO ₃	37.4	50.0
Nalco (Nalco 471)	3.5; Co	----	12.5; MoO ₃	61.2	----
Peter Spence	2.5; CoO	----	14.0; MoO ₃	57.9	66.0

The operating conditions for the catalyst comparison runs listed in the above table are shown below.

Operating temperatures of 800°F and 750°F

Operating pressure of 1000 psig

Liquid hourly space velocity of 0.5 ml oil/hr-ml catalyst

Hydrogen flow rate of 5,000 SCF/bbl oil

Feedstock was a California heavy gas oil containing 0.238 weight percent nitrogen, 2380 ppm nitrogen. (Feedstock No. 1)

All of these commercial catalysts are supported on alumina supports. The L.H.S.V. used during the catalyst comparison tests was selected as 0.5 on the basis of the results obtained during the initial tests and a knowledge of reasonable commercial operating liquid hourly space velocities. The operating temperature was selected using the same considerations. Prime consideration was also given to keeping the conversion in the 10 to 90 percent range.

Of the commercial cobalt molybdate, nickel cobalt molybdate, and nickel molybdate catalysts tested, Houdry "C" cobalt molybdate and Cyanamid's (HDS-3) nickel molybdate seemed to be among the most effective hydrodenitrogenation catalysts (See Table I). Other noticeable results were the wide variation in the various commercial catalysts' activity for hydrodenitrogenation and that traces of NiO on cobalt molybdate catalysts seemed to enhance their hydrodenitrogenation ability. The commercial catalysts were presulfided before use for maximum activity. It was decided that the developed and prepared hydrotreating catalysts would be compared with the Houdry "C" cobalt molybdate catalyst since

this catalyst seemed to be as active as any of the commercial hydro-treating catalysts of the cobalt molybdate, nickel cobalt molybdate, or nickel molybdate types. The effect of the operating variables, space velocity and temperature, on the nitrogen removing capability (activity) of a commercial cobalt nickel molybdate catalyst was determined using the Filtrol (FG 500-8) catalyst. Although this is not the most active catalyst of the commercial cobalt/nickel molybdate type, it was the most readily available catalyst and is representative of the cobalt/nickel molybdate catalysts tested. The results of these tests are shown in Figures 6A and 7A. As noted in these Figures, space velocities between 0.5 and 5.0 were used along with temperatures between 700°F and 800°F. The results were as expected. That is, the catalyst activity decreased with increasing L.H.S.V. and increased with increasing temperature. These tests indicate that high temperatures and low liquid hourly space velocities in conjunction with a highly active catalyst will be required in order to remove most of the nitrogen from high nitrogen content petroleum gas oils.

While the aforementioned work was being conducted, the results of these tests, the literature, and thermodynamic calculations were studied in an attempt to uncover a potential hydrotreating catalyst.

Statistical Analysis of the Data

Utilizing the data from Runs 1, 2, 3, 4, 5, 9, 15, 25, 26, and 27, a statistical analysis was made in order to determine an estimate of the

difference in catalyst activity (percent conversion) necessary in order to be considered as being significant (6, 17, 32, 39). That is, an analysis was made in order to determine what difference in nitrogen conversion is required in order to indicate a significant difference in catalyst activity. Runs 1, 2, 3, 4, and 5 differ from the other runs, in operating condition other than catalyst employed, only in that the H_2 flow rate was 8,000 SCF/bbl instead of 5,000 SCF/bbl. Figure 4A indicates that this change in H_2 flow rate is not significant as does a statistical analysis of the results of Runs 1, 2, 3, 4, 5, and 9. Therefore, an analysis of variance for one-way classification (Ref. 39) with unequal replication and equal subsample numbers was performed on these data. Runs 1, 2, and 3 are replication tests as are runs 4, 5, and 9. The other runs were not duplicated. All tests had two determinations per test run. Each sample was analyzed twice and the two conversion values obtained for each test run are the average of the conversion data obtained after lineout on the first and second analysis of each sample, respectively.

The resulting analysis of variance table for these tests is given below.

TABLE II. ANALYSIS OF VARIANCE RESULTS FOR EXPLORATORY TESTS

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F
Treatments	5	2370.26	474.05	644.97
Experimental Error	4	2.94	0.735	6.50
Sampling Error	10	1.13	0.113	---
Total	19	2374.33	---	---

$$S_{\bar{d}} = \sqrt{S^2 \left(\frac{1}{r_i} + \frac{1}{r_j} \right)} = \sqrt{0.735 \left(\frac{r_i + r_j}{r_i r_j} \right)}$$

where

r_i and r_j are the number of observations in the two means being compared.

$S_{\bar{d}}^{t_{0.05,4}}$ = the least significant difference for the means being compared at the 95 percent confidence level.

These results indicate that there are significant treatment (catalyst) differences since $F_{0.01}$ with 5 and 4 degrees of freedom is much less than the calculated value of 644.97. $F_{0.01}$ with 4 and 10 degrees of freedom is less than 6.50. Therefore, there is variation in addition to

that among the subsamples. That is, replicated tests vary due to sources of variation other than or in addition to the chemical analysis of the samples.

The results of this statistical analysis of the exploratory test data yielded no unexpected results and does not change any of the conclusions or statements made to this point in the research work. The author realizes that these data could be analyzed further, statistically, but feel that further statistical analysis of this exploratory test data is unwarranted. The main purpose of the analysis performed was to gain an estimate of the difference in conversion between test runs that is necessary in order to indicate a significant difference in catalyst activity. This would be very useful in analyzing the preliminary catalyst preparation test results.

The results presented in Table II indicate that a difference of 2.38 percent in the nitrogen conversion would be required to indicate a significant difference in catalyst activity, at the 95 percent confidence level, for $r_i = r_j = 1$. This assumes that each catalyst is tested only once. That is, the least significant difference would be $S_{d, 0.05, 4}^t$ or $(0.8575) (2.776) = 2.38$ percent. If the difference is 2.38 percent or greater, we can be at least 95 percent confident that the two catalysts tested have different activities.

Catalyst Life Investigation

A thermodynamic feasibility study, based on an assumed mechanism, of various metals as effective hydrodenitrogenation and hydrodesulfurization catalysts indicated the possibility that tungsten disulfide, along with various other metal compounds, might possibly be an effective hydrodenitrogenation catalyst. Therefore, it was decided that tungsten would be evaluated as a hydrodenitrogenation catalyst.

It should be noted that the Shell Oil Company has previously used a catalyst consisting of pellets containing 48 percent tungsten, 20 percent nickel, and 25 percent sulfur for hydrotreating petroleum fractions, the remaining percentage being iron, carbon, and unidentified material. Shell has discontinued use of this tungsten nickel sulfide catalyst. Recently the Harshaw Chemical Company has started to offer commercial nickel, in the reduced form, tungsten sulfide catalysts for hydrocracking and other hydrotreating purposes. One of these catalysts contains 6 percent nickel and 19 percent tungsten and is available on either an alumina or silica alumina base. The other containing 4.5 percent nickel and 9.5 percent tungsten is available on an alumina base.

Before setting up the research plan for the development of a tungsten type hydrodenitrogenation catalyst, the literature and U.S. Patents were reviewed for helpful information in deciding upon the best research plan. At the same time it was decided that the Harshaw tungsten type catalysts would be evaluated for hydrodenitrogenation purposes. Therefore, a test run was started (Run No. 37) utilizing Harshaw's

Ni-4401-E hydrocracking catalyst containing six (6) percent nickel, in the reduced form, and nineteen (19) percent tungsten as the sulfide on a silica-alumina support. From personal correspondence with R. J. Wensink, Catalyst Representative for the Harshaw Chemical Company, it was determined that this catalyst contains approximately fifty (50) percent silica (S_iO_2) by weight. The results of an extended test run utilizing this catalyst are discussed below.

The results of this test are presented in Figures 8A and 9A. As noted in these figures, the test was started utilizing the "standard" (page 100) operating conditions, except that the catalyst was not presulfided since it was received in that form and the manufacturer did not recommend that the user presulfide the catalyst. The feedstock, Feedstock No. 2, contained 1810 ppm nitrogen and 0.58 wt.% sulfur and had a boiling range of 540-820°F. Initially, the catalyst removed approximately 97.5 percent of the nitrogen from this gas oil.

After 60.5 hours on stream, the feedstock was switched to Feedstock No. 4. The properties of this oil, which contained 2560 ppm nitrogen, are given in Table I-A. The catalyst removed approximately 88.5 percent of the nitrogen from this gas oil.

After 50 hours of operation utilizing Feedstock No. 4, or 110.5 total hours on stream, the feedstock was switched back to Feedstock No. 2. At this time the catalyst removed about 91 percent of the nitrogen from this gas oil. When the temperature was reduced to 750°F, the

nitrogen conversion was reduced to 79 percent. When the temperature was again raised to 800°F, the conversion obtained was 92.5 percent. Therefore, after six (6) days on stream the conversion had dropped about 5 percent.

After 146 hours (total) on stream, the feedstock was again switched. Feedstock No. 5, which contains 3350 ppm nitrogen, was fed to the reactor. Approximately 82 percent of the nitrogen was removed for this gas oil by the Ni-4401-E catalyst.

Upon returning to the original feedstock, after 60 hours of operation utilizing Feedstock No. 5, it was found that the catalyst still removed nearly 90 percent of the nitrogen from this feedstock. Therefore, after 10 days of operation the catalyst still removed 90 percent of the nitrogen from Feedstock No. 2.

Since catalyst evaluation studies need catalyst-life data, which are expensive to obtain, to have much meaning, it was planned that an extended catalyst-life test would be conducted during this research project. It was therefore decided at this time that since 10 days of operation had already been completed utilizing the Ni-4401-E catalyst and its activity was still high, that an extended -- possibly 90-day -- catalyst-life test on a tungsten type hydrodenitrogenation catalyst should be conducted at this time. Consequently, this test run was continued for another 80 days in order to obtain this valuable catalyst-life information. This also afforded the author an opportunity to

further review the literature for helpful catalyst preparation and development information.

The operating conditions were maintained at the original conditions until 62.5 days of total test duration had passed, with the results shown in Figure 8A. At this time the catalyst was still removing 74.5 percent of the nitrogen from the gas oil. The temperature was raised to 820°F at this point in the test and maintained there for the remaining 27.5 days of the test. The conversion which increased to 85 percent upon the initial temperature rise dropped to below 80 percent within approximately five (5) days. But at the end of the test the nitrogen removal was still around 74.5 percent.

It is felt that this test proved that a tungsten type hydrodenitrogenation catalyst would have a long catalyst life if used for hydro-treating high nitrogen content petroleum gas oils at conditions as severe or less severe than those used herein.

Since this catalyst (Ni-4401-E) was developed as a hydrocracking catalyst it was feared that possibly at the severe hydrotreating conditions employed in Run No. 37, excessive cracking of the feedstock might result in the "coking" and resulting deactivation of the catalyst. This was especially feared upon learning of the high silica content of the catalyst. But the catalyst did not seem to cause excessive cracking during the extended run. This was evidenced by the condition of the catalyst after the test and the relatively slow catalyst deactivation rate.

A material balance conducted over approximately a ten-day period yielded the following results. This was conducted from the eightieth to the ninetieth day of the test. During this time a 95.5 percent (by weight) recovery of the feedstock was obtained. The A.P.I. gravity of the feedstock was approximately 24 (Table I-A) and that of the product was 29.5.

The results of an analysis of the feedstock and product, (performed by the Continental Oil Company at Ponca City, Oklahoma), obtained from a sample taken during the fiftieth to the fifty-second day of the test are presented in Table VII-A. In general, it is noted that the feedstock analysis performed by Continental Oil Company agrees quite well with that presented in Table I-A. As can be noted from the data in this table (Table VII-A), the percent nitrogen conversion was approximately 77.2 percent at the time this sample was taken. This is in close agreement with the results obtained by the author (see Figure 8A). Also, a very close agreement between Continental Oil Company and the author is noted on the nitrogen content of the feedstock. As noted in Table VII-A, the sulfur conversion is still 96.7 percent at the end of nearly 52 days of reactor operation. This is not an unexpected result because of the relative ease of sulfur removal as compared to the removal of nitrogen from petroleum fractions.

It has been noted by many investigators (Refs. 10, 15, 36, 38) that the nitrogen content (concentration) of a feedstock can significantly

affect the nitrogen conversion obtained at a given process condition. Also, it has been noted (Ref. 15) that in petroleum fractions from the same crude source, that the higher boiling range fractions of the crude contain a higher percentage of nitrogen than lower boiling fractions, in general. It is also known that the type of nitrogen compound or compounds present in the oil significantly affect its ease of removal (Refs. 10, 15, 36, 38). It is readily understood that similar boiling fractions from different crude sources may have quite different nitrogen concentrations (Ref. 3), or, that even if they have similar nitrogen contents the ease of removing the nitrogen from these two oils could be quite different because of the difference in nitrogen compounds that the two oils may contain.

With the above discussed material in mind, it is interesting to note the results obtained with the different feedstocks employed in Run 37. As noted in Table I-A, the higher the boiling range of the feedstock employed, the higher was its nitrogen content and the more difficult was the job of removing the nitrogen from the gas oil.

As noted in Table VI-A, the effect of water washing the sample prior to analysis to remove any free nitrogen was tested during this test run. The results indicated that the effect of water washing the product sample, prior to analysis, on the sample's nitrogen content is negligible.

After the completion of the extended ninety-day test, two short duration tests were made at the same operating conditions. These tests, Runs No. 38 and 39, confirmed the high activity of the Ni-4401-E catalyst and further established the high repeatability of the testing procedure.

Table VIII-A contains the results of gas analyses performed on the effluent gas from the reactor during Run No. 37 and Run No. 38. The analysis from Run No. 37 was taken on the eighty-sixth day of the test. The gas sample from Run No. 38 was taken approximately two and one-half days into the test. The most significant difference between the samples is that the sample taken at two and one-half days into the test run contains about two percent less hydrogen and consequently, about two percent more light hydrocarbon gases than the sample taken near the end of Run No. 37. In both cases the gas contains greater than 90 percent hydrogen and 7 to 9 percent light hydrocarbon gases from the cracking taking place. The gas analyses were performed by the Yapuncich, Sanderson & Brown Laboratories at Billings, Montana by chromatographic analysis.

In order to obtain some indication of the importance of the catalyst support on its resulting activity, test Run No. 40 was conducted. The catalyst used for this test was Ni-4403-E. This catalyst is similar to the Ni-4401-E catalyst except that the support is alumina instead of silica-alumina. The same operating conditions as were employed in tests 37, 38, and 39 were utilized. Only ninety-one percent nitrogen removal

was obtained during this test. This is approximately 6.5 percent lower than was obtained with a similar catalyst on a silica-alumina support. It is believed that this difference in catalyst activity can be attributed to the difference in the catalyst support used.

A comparison of Harshaw's hydrocracking catalyst (Ni-4401-E) containing 6 percent nickel in the reduced form and 19 percent tungsten as the sulfide on a silica-alumina support was also made with Houdry "C" cobalt molybdate catalyst. Houdry "C" catalyst was the most active cobalt/nickel molybdate catalyst tested. "Standard" operating conditions were used except that the Ni-4401-E catalyst did not need to be presulfided. The feedstock used was Feedstock No. 3 which contains 3190 ppm nitrogen and the following results were obtained. The Houdry "C" catalyst removed 79.8 percent of the nitrogen from the gas oil while the nickel tungsten sulfide catalyst removed 92.2 percent of the nitrogen from the gas oil. These results clearly indicate that a thorough study of tungsten as a hydrodenitrogenation catalyst is warranted. Also, the superiority of a nickel tungsten catalyst over a cobalt molybdate catalyst for hydrodenitrogenation was indicated.

PRELIMINARY CATALYST PREPARATION TESTS

The results that can be obtained from a thorough study of a presently used catalyst for a specific purpose (process) is illustrated very well in U.S. Patent No. 3,114,701 issued in December of 1963 (Ref. 20). In this patent the increased denitrogenation ability of nickel

molybdate catalysts on an alumina support in the range containing 4-10 percent nickel together with 15.5-30 percent molybdenum by weight is noted over the conventionally used nickel molybdate hydrotreating catalysts. Conventional nickel molybdate and cobalt molybdate catalysts usually contain only about 10 to 12 percent by weight (total) of the metals. These conventional catalysts were originally developed for hydrodesulfurization purposes.

U.S. Patent No. 3,114,701 clearly indicates the results that may be obtained by the thorough study of a general hydrotreating catalyst for a specific purpose. In this case, a conventional desulfurization catalyst was studied thoroughly and improved to make it a more active hydrodenitrogenation catalyst. Therefore, based on the experimental results obtained from the exploratory test conducted during this research and a simultaneous literature review, a thorough study of tungsten as a hydrodenitrogenation catalyst seemed warranted.

Before setting up the research plan for the development of a tungsten type hydrodenitrogenation catalyst, the literature and U.S. Patents were reviewed for helpful information in deciding the most appropriate research plan. The most pertinent results of this review of available material, which was very fruitful, are presented on pages 13 through 18. The research plan constructed for this phase of the research is presented on pages 34 through 36.

All of the preliminary Catalyst Preparation Tests were conducted utilizing the same operating conditions. The catalyst pretreatment and reactor startup procedures were different for some of these tests but only for the purpose of studying the effect of these variables on the catalyst activity. Unless otherwise noted, the operating conditions, catalyst pretreatment, and reactor startup procedure noted on page 100, as "standard operating conditions" were utilized. Feedstock No. 3 (Table I-A) was used for all of these tests.

Catalyst Preparation Feasibility

Since catalyst preparation and manufacture is sometimes considered to be more of an art than a science, it was felt that the first two catalyst preparation test objectives should be accomplished early in the experimental plan.

Figure 10A presents the results of the initial catalyst preparation tests conducted in order to determine if an active hydrodenitrogenation catalyst of the type desired could be prepared in the laboratory. The catalyst preparation procedures described on pages 30 to 32 were employed. The results presented in this Figure indicate that an active catalyst of the type desired can be prepared in the laboratory. All of these catalysts were sulfided as per the "standard" manner.

The pertinent "initial" preliminary Catalyst Preparation test results presented in Figure 10A are:

- (1) When Feedstock No. 3 is treated at the "standard operating conditions" utilizing only an alumina catalyst support material with no impregnated metals, only 3.5 percent of the nitrogen was removed from the gas oil.
- (2) When 12.5 Wt.% nickel was impregnated on an alumina catalyst support, approximately 50 percent of the nitrogen was removed from the feedstock under these same operating conditions.
- (3) With 14.5 Wt.% tungsten impregnated on this alumina support, 75 percent removal of the nitrogen can be obtained under the same operating conditions.

These results seem favorable, especially when compared with the results obtained during Run No. 42. As noted in Figure 10A, the Houdry "C" cobalt molybdate catalyst (Run No. 42) removed 80 percent of the nitrogen from the same gas oil under identical operating conditions. Therefore, the preparation of an active tungsten catalyst in the laboratory seemed favorable, especially when the possibility of promoting the catalyst with known hydrotreating catalyst promoters was considered. Also, the possibility of finding a more adequate support for the tungsten and optimization of the amount of material (metals) on the support could possibly give a more active catalyst than the one tested in this case.

Effect of Metal Impregnation Order on Catalyst Activity

In Figure 11A, the results of two tests conducted in order to determine if the order of metal impregnation onto the catalyst support affects its activity are presented. As noted in this Figure, the difference in the mean conversions obtained during the tests was 2.5 percent. The support upon which the tungsten was impregnated first appears to result in the most active catalyst. As noted in Figure 11A, the two catalysts are both on the same alumina support and are of nearly the same composition. Again, these catalysts were sulfided in the standard manner.

On the basis of the results of the statistical analysis of the Exploratory Test data, the difference in the two catalysts' activities would be deemed significant. A difference of 2.38 percent or greater is required for statistical significance at the 95 percent confidence level on the basis of the statistical analysis of the Exploratory Test results. Application of results obtained from a statistical analysis of the Experimental Design test data indicate that the 2.5 percent difference in catalyst mean conversion is not significant at the 95 percent confidence level. Based on these tests, a difference of >2.5 percent is required in the mean conversions for a significant catalyst activity difference. It therefore appears to be questionable if metal impregnation order affects the resulting catalyst activity.

It was noted during the catalyst preparation that when the nickel was impregnated onto the support first, some of the nickel seemed to be

leached from the support during impregnation of the tungsten onto the support. For this reason, and the apparent difference in the two catalysts' activities, future catalysts were prepared if possible with the tungsten impregnated onto the support first.

A comparison of the results presented in Figures 10A and 11A indicates that approximately a 6 percent increase in the tungsten catalysts' hydrodenitrogenation activity results from the use of 5 percent nickel as a promoter on this tungsten catalyst, at least when Girdler's T-126 alumina support is employed. Also, it should be noted that the nickel promoted tungsten on an alumina support catalyst is apparently as active as the Houdry "C" cobalt molybdate catalyst for hydrodenitrogenation. Neither of these catalysts is as active as Harshaw's Ni-4401-E nickel tungsten sulfide hydrocracking catalyst on a silica-alumina support. This is evident from the results of tests Nos. 41 and 42 in which the Ni-4401-E and Houdry "C" catalysts were tested, respectively.

It should be noted that an analysis of catalyst conversion "lineout" data from early catalyst preparation tests indicated that both the "lineout" time and characteristics of the nickel tungsten type catalysts are similar to those of the commercial cobalt/nickel molybdate catalysts.

Effect of Catalyst Preparation Repeatability and Test Run Duplication on Catalyst Activity Determination

Figure 12A presents the results of tests conducted in order to determine the repeatability of catalyst preparation and test run duplication

on the catalyst's activity for hydrodenitrogenation. The results are for the preparation and testing of two separate batches of tungsten catalyst promoted with nickel on an alumina base. As noted in the Figure, the preparation of tungsten type catalysts in the laboratory is reasonably repeatable. The results of these tests also indicate that the repeatability of test run duplication is reasonably good. These catalysts were sulfided prior to use in the "standard" manner.

Catalyst Promoter Evaluation

In Figure 13A, the results of tests conducted in order to evaluate conventional hydrotreating catalyst promoters for promoting the tungsten type catalyst are presented. The results indicate that nickel is the best promoter for the tungsten catalyst when it is used for hydrodenitrogenation. For these trial runs some of the alumina catalyst support obtained from Nalco Chemical Company (Table II-A) was impregnated with 20.2 Wt.% tungsten. These pellets were then split into four separate batches. One batch was impregnated with nickel, one with cobalt, one with molybdenum, and the other was not impregnated with any promoter. Cobalt was impregnated from a cobalt nitrate solution. Molybdenum was impregnated from an ammonium molybdate solution. In each case, the resulting catalyst contained approximately 8 to 9 percent by weight of the promoter. Calcining of these pellets to obtain the oxides was, of course, necessary. The catalysts were presulfided in the "standard" manner. That nickel is the best promoter is clearly indicated. Cobalt and molybdenum increased the activity of the tungsten catalyst by an almost insignificant amount.

The nickel-promoted catalyst's activity was increased by approximately 10 percent. Therefore, nickel was chosen as the promoter to be used in the tungsten type hydrodenitrogenation catalyst development effort.

Another aspect of the results to date is noted by making a comparison of the results presented in Figures 10A, 12A, and 13A. It is noted that the activity of the nickel tungsten catalyst on both alumina supports T-126 and 65-2542 is nearly identical. But the unpromoted tungsten catalyst on the T-126 support was more active than the unpromoted tungsten on the 65-2542 support. This difference could possibly be the result of metal content differences and/or support differences.

Effect of Catalyst Pretreatment on Catalyst Activity

Figure 14A presents the results of tests conducted in order to determine the effect of various pretreatment methods on the nickel tungsten catalyst activity. These trial tests were made using catalyst from the same batch of catalyst. The results presented indicate that presulfiding the catalyst with an 80 percent hydrogen - 20 percent hydrogen sulfide mixture, by volume, at 650°F, at the rate of 2 standard cubic feet of gaseous mixture per hour until sulfur equal to one-half the weight of the catalyst was passed over the catalyst is as effective as any of the pretreatment methods employed. This is the "standard" presulfiding treatment that had been used previously and it was used in the remaining catalyst testing. As noted in this Figure (Figure 14A), decreasing the sulfiding temperature to 350°F or increasing the amount of sulfur passed

over the catalyst during the presulfiding period does not significantly affect the catalyst activity. Also, presulfiding the catalyst by any of the above methods resulted in an increase of approximately 10 percent in the resulting catalyst activity over that of the non-presulfided catalyst.

Presulfiding the catalyst with a mixture of carbon disulfide (CS_2) in cyclohexane is also a fairly effective means to activate the catalyst as noted in Figure 14A. In this case, a 5 percent by weight sulfur solution made by diluting CS_2 in cyclohexane was employed. This feedstock was fed to the reactor operating at the "standard operating conditions", except that the temperature was $650^\circ F$. This treatment was continued until sulfur equal to one-half the weight of the catalyst was passed over the catalyst.

An attempt was made to nitride the catalyst using a solution of pyridine in cyclohexane. A solution containing 5 percent by weight nitrogen was employed. It was made by diluting the pyridine in cyclohexane. The pretreatment was carried out in a manner similar to that employed for the CS_2 in cyclohexane pretreatment. That is, at the same condition, until nitrogen equivalent to one-half the weight of the catalyst was passed over the catalyst. The results of this pretreatment did not significantly affect the catalyst activity, as noted in Figure 14A.

Tests, Runs No. 64-P, 65-P, and 66-P were conducted in order to determine the best manner in which to start the test runs when utilizing a nickel tungsten catalyst on a silica-alumina support. Three different reactor startup procedures were evaluated. The procedures tested were:

- (1) Standard procedure (page 100).
- (2) Standard procedure except that the run was started with the catalyst at 650°F when contacted with the initial feedstock flow.
- (3) Standard procedure except that the catalyst was subjected to a reducing atmosphere, hydrogen at 650°F after sulfiding. H₂ at the "standard operating conditions", flow rate and pressure were employed for a 10-hour period.

These reactor startup procedures were tested because many hydrotreating manufacturers do not recommend initial contact of their catalysts with the feedstock while the catalyst is at elevated temperatures. This may possibly result in the initiation of cracking by the catalyst and a resulting loss in the catalyst activity, especially in the case where the support is of the silica-alumina type, as employed herein. The reducing atmosphere was employed in an attempt to determine if the nickel could possibly be reduced and result in an increase in the catalyst activity. The results obtained indicated very little difference, if any, in the catalyst activity (Table VI-A). The run conducted at "standard conditions", Run No. 64-P, resulted in the highest nitrogen conversion.

Of course, this startup procedure was utilized thereafter, as previously.

Catalyst Support Evaluation

Figure 15A presents the results of tests conducted in order to evaluate various commercial alumina and silica-alumina supports. These tests were made to evaluate the various supports by keeping the weight percent of the metals, tungsten and nickel, on the support nearly constant. The difference in these catalysts' composition are not significant enough to cause catalyst activity differences, as will be noted in the Experimental Design test results. The best pretreatment method and impregnation order, as previously determined, were used for all of these catalysts. The properties of the supports as received are shown in Table III-A.

The most noticeable results from these tests were:

- (1) That, in general, use of a silica-alumina support resulted in a more active catalyst than the use of an alumina support.
- (2) That, in general, there was little difference between the various alumina supported catalysts as a group or between the various silica-alumina supported catalysts as a group ... even though the physical properties of the various supports varied markedly.

It was also noted that the silica-alumina supports produced catalysts whose activities were near that of Harshaw's Ni-4401-E hydrocracking catalyst which contains 6 percent nickel in the reduced form and 19 per-

cent tungsten as the sulfide on a silica-alumina base containing approximately 50 percent silica (SiO_2). The silica-alumina supports utilized herein contained approximately 7 percent SiO_2 , as noted in Table III-A. The reason for limiting the silica content of the supports tested to this low value was discussed on pages 16 and 17. The catalysts tested all contained approximately 5 percent nickel and 15 percent tungsten.

The second result, above, seems somewhat surprising in view of the fact that there were large differences in the densities and pore volumes of the various supports tested. As noted in Table III-A, Al-1602-T support is much denser than the Al-1802-E support. Therefore, when compared on the L.H.S.V. basis, a volume basis, the more dense catalyst will contain much more tungsten and nickel in the same volume of reactor. If the catalysts have the same weight percent of metals on them, as was the case here, it would seem that the more dense catalyst would possibly be more active when compared on this volume basis since it contains more of the metals on a total weight basis. This was not found to be the case. It should be noted that the volume basis, L.H.S.V., used for the catalyst comparison tests herein is the common basis employed in the petroleum industry. Therefore, for the experimental design portion of this research work, a support of the silica-alumina type with low bulk density was employed. This should result in a catalyst of the same activity on the volume basis used to compare the catalysts while using less total metal. Of course, this would be the most economical support to

use. Also, the use of this support makes it possible to absorb more impregnating solution per impregnation and more total material without plugging the catalyst support pores because of the higher pore volume of the support. The support Al-1802-E was therefore used for the experimental design. The high pore volume of this support made it easy to vary the metal content of the support (catalyst) over a wide range for the experimental design which was used to optimize the weight percent of the various metals, nickel and tungsten, on the support for a catalyst of maximum hydrodenitrogenation ability.

The preliminary Catalyst Preparation Tests were conducted utilizing 15 to 20 percent tungsten together with 5 to 10 percent promoter, if any, on the catalyst support. The reasons for choosing these ranges of metal content(s) were:

- (1) The results obtained during the Exploratory Testing using Harshaw's nickel tungsten catalyst.
- (2) Commercially available hydrotreating catalysts that were developed originally for hydrodesulfurization contain only 10 to 12 percent (total) of impregnated metals. But Reference 20 notes the increased activity of this type of catalyst for hydrodenitrogenation in the range containing 20 to 40 percent (total) of impregnated metals.

Higher metal contents were not utilized because of the possibility of

plugging the pores of the catalyst support. This could result in a decrease in the catalyst activity due to the plugging of the pores.

EXPERIMENTAL DESIGN AND CATALYST EVALUATION TESTS

Experimental Design

In an attempt to determine the "optimum" amount of nickel (promoter) and tungsten (primary metal component) that should be impregnated onto the support (Al-1802-E) to yield a catalyst of maximum hydrodenitrogenation activity, an experimental design was employed. The method of response surfaces was used to determine the effect of these quantitative factors on the catalyst activity. The second order design employed yielded a polynomial (quadratic) approximation of the true response surface.

The second order design chosen for this work was the "Central Composite Rotatable Design" (Ref. 9). In a rotatable design, the standard error is the same for all points that are the same distance from the center point of the design. As noted in Ref. 9, this property is a reasonable one to adopt for exploratory work in which the experimenter does not know in advance how the response surface will orient itself with respect to the X-axes. Consequently, he has no rational basis for specifying that the standard error should be smaller in some directions than in others.

The basic layout of the design used is shown below in Figure 2. The design points are shown in the coded scale. The relationship be-

tween the coded scale and the actual scale values are shown in Table III. Design Point One was tested five times. For example, Design Point Four which is $(-1, -1)$ in the coded scale and $(3.46, 8.93)$ in the actual scale should be a catalyst with 3.46 percent nickel (by weight) and 8.93 percent tungsten (by weight). All design points except Design Point One were tested only once.

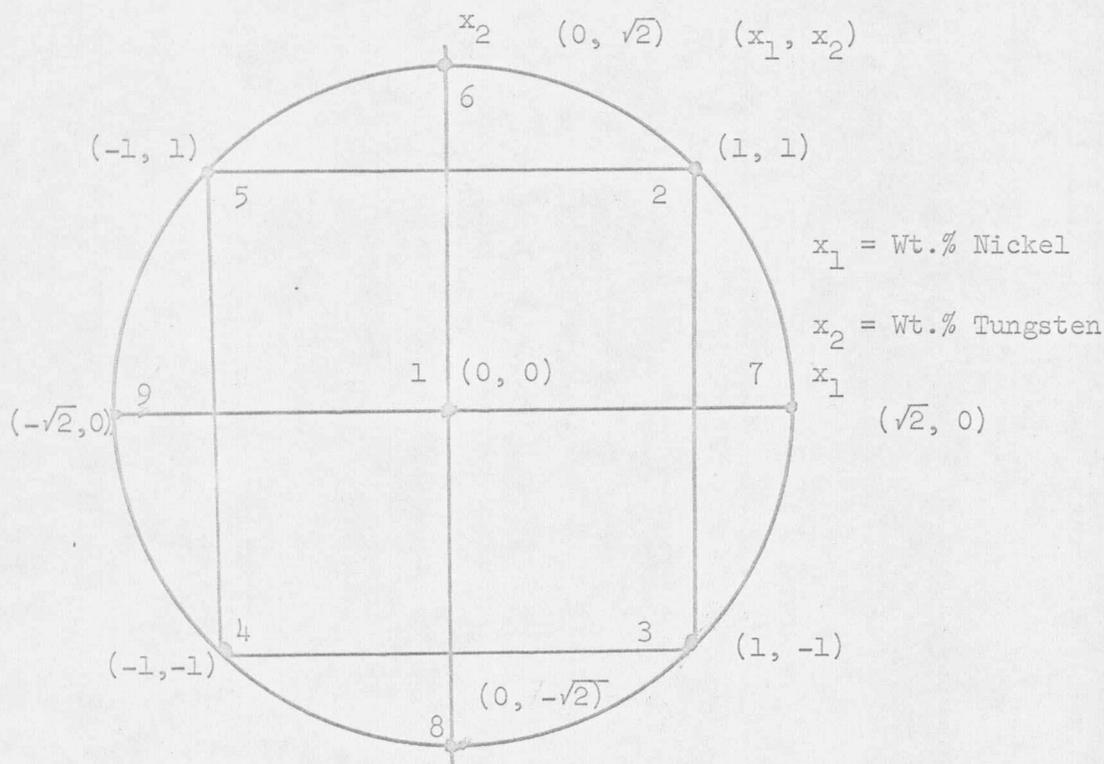


Figure 2. Experimental Design Layout.

TABLE III. EXPERIMENTAL DESIGN TEST POINTS

<u>Design Point</u>	<u>Coded Scale Value</u>	<u>Actual Desired Scale Value</u>
1	(0, 0)	(7.00, 16.00)
2	(1, 1)	(10.54, 23.07)
3	(1, -1)	(10.54, 8.93)
4	(-1, -1)	(3.46, 8.93)
5	(-1, 1)	(3.46, 23.07)
6	(0, $\sqrt{2}$)	(7.00, 26.00)
7	($\sqrt{2}$, 0)	(12.00, 16.00)
8	(0, $-\sqrt{2}$)	(7.00, 6.00)
9	($-\sqrt{2}$, 0)	(2.00, 16.00)

As noted in Table III, the nickel content, X_1 , of the catalysts tested in the experimental design ranged from 2.00 to 12.00 weight percent. The tungsten content, X_2 , of the catalysts ranged from 6.00 to 26.00 percent (weight percent). Catalysts were prepared with compositions near the desired ones and were tested. The catalysts were prepared with compositions as near as possible to the actual scale desired value. The range of nickel and tungsten catalyst contents were chosen for study on the basis of the experimental results obtained to date and a knowledge of the maximum amount of metal that can be impregnated onto supports of the type being employed without causing excessive plugging of the catalyst's pores which would result in a decrease in the catalyst activity. As noted in References 20, 31, and others, the total metal on catalyst supports of the type used herein should not exceed the 25 to 35

percent (by weight) range. If higher metal contents are used, plugging of the catalyst pores and decreased catalyst activity will probably result.

As noted previously, the center point of the design was tested five times. The purpose of this was twofold. It provided four degrees of freedom for estimating the experimental error and it determines the precision of the estimated conversion at and near the center of the design. If there were many replications of the center point, the standard error would be low at the center and increase rapidly as we moved away from the center. With only one or two replications of the center point, on the other hand, the standard error may be greater at the center point than at the other experimental points. The number of center point replications used, (five), provides that the standard error of the predicted conversion is approximately the same at all points tested.

Since this experimental design assumes that the experiment is to be randomized, the different treatment combinations (experimental points) were applied (tested or carried out) in a randomized order.

It should be noted that the polynomial (quadratic) expression generated should not be extrapolated outside of the design's limits; i.e., it should be applied only within the region of X_1 and X_2 covered by the experiment. Any predictions made from the polynomial about the response outside this region should be verified by experiment before putting reliance on them. Catalysts were prepared in the method described

earlier in this thesis, with nickel and tungsten contents suitable for the "Central Composite Rotatable Design" described above. Table IV below presents a comparison between the desired design metal contents of the catalysts and the actual metal contents of the catalyst tested. As noted previously, the prepared catalysts had compositions very close to the desired compositions.

TABLE IV: COMPARISON OF THE DESIRED AND ACTUAL METAL CONTENTS OF THE DESIGN'S CATALYSTS

Design Point	Desired Values		Actual Values	
	Weight Percent Nickel	Weight Percent Tungsten	Weight Percent Nickel	Weight Percent Tungsten
1	7.00	16.00	7.5	15.1
2	10.54	23.07	10.2	23.1
3	10.54	8.93	10.8	9.0
4	3.46	8.93	3.5	9.0
5	3.46	23.07	3.5	23.0
6	7.00	26.00	6.8	25.8
7	12.00	16.00	11.2	15.9
8	7.00	6.00	7.0	6.0
9	2.00	16.00	2.5	16.0

All of the catalysts were tested at the same "standard operating conditions" noted in Table V-A, on page 100. The randomized order of

testing is noted below in Table V. There are nine points but thirteen total tests in the design.

TABLE V. EXPERIMENTAL DESIGN POINTS TEST ORDER

<u>Test Order</u>	<u>Design Point</u>
1	9
2	8
3	1
4	2
5	6
6	4
7	1
8	3
9	1
10	5
11	7
12	1
13	1

The conversion of nitrogen obtained utilizing each catalyst was taken as the average of the conversion that was obtained from the samples taken after 12 or more hours of reactor operation. The tests were generally between 24 and 48 hours in length. Statistical analysis of the conversion data taken after 12 hours of reactor operation indicated that the conversion was independent of the run length for these tests; i.e.,

the catalyst lineout time and characteristics of the nickel tungsten catalysts were similar to those of the cobalt/nickel molybdate catalysts.

In order to determine if significant differences existed between the treatments (catalysts) tested in the "Central Composite Rotatable Design", the experimental data from the design were analyzed first by the method of Analysis of Variance. The design is characteristic of a completely random design with one-way classification. In an attempt to determine if significant differences existed between repeated treatments other than that due to the chemical analysis of the samples, all samples were analyzed in duplicate. Therefore, for each test conducted in the design, two separate conversion values were obtained -- one from each analysis.

The experimental design used in determining the "optimum" amount of nickel and tungsten that should be impregnated onto the support to yield a catalyst of maximum hydrodenitrogenation activity was basically a completely randomized design; (i.e., the tests were carried out in a randomized order and the experimental units were essentially homogeneous.)

Preliminary analysis of the data from the "Central Composite Rotatable Design" using the principles of analysis of variance for one-way classification and equal subsample numbers is summarized in the following Analysis of Variance Table.

TABLE VI. EXPERIMENTAL DESIGN
 (Analysis of Variance: One-Way Classification with
 Unequal Replication and Equal Subsample Numbers.)

<u>Source of Variation</u>	<u>Degrees of Freedom</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F</u>
Treatments	8	186.48	32.31	15.24
Experimental Error	4	6.12	1.53	8.50
Sampling Error	13	2.34	0.18	----
Total	25	194.94	----	----

Using this Analysis of Variance Table (Table VI) the null hypothesis was tested that there was no difference in the treatment (catalysts) tested; i.e., the hypothesis was tested that there was no significant activity difference in the catalysts tested. This hypothesis was rejected. In fact, we can be at least 99 percent confident that there are activity differences in the catalysts tested. ($F_{0.01}$ with 8 and 4 degrees of freedom is 14.8.)

Experimental error may or may not contain variation in addition to that among the subsamples (sampling error). This will depend upon the environmental differences that exist from run to run. If the two mean squares for experimental error and sampling error were of the same order of magnitude, then any variation among like treatments could be attributed entirely to the sampling error (chemical analysis). The experimental error is usually larger than the sampling error since it contains an

additional random source of variation; that is, environmental differences from run to run. If $F_{\text{calculated}}$ is greater than F_{tabled} with 4 and 13 degrees of freedom where

$$F_{\text{calculated}} = \frac{\text{experimental error mean square}}{\text{sampling error mean square}}$$

and F_{tabled} is the tabled F value, then there are real sources of variation in similar tests other than those due to the chemical analysis (sampling error).

$F_{\text{calculated}} = 8.50$ and is greater than $F_{0.01}$ (with 4 and 13 degrees of freedom). Therefore, we are at least 99 percent confident that an additional source of variation other than sampling error caused by environmental differences exists from run to run.

The standard error of a treatment mean is $S_{\bar{x}} = 0.391$ percent and the standard error of a difference between treatment means is $S_{\bar{d}} = 0.958$ percent. The meaning of these quantities, $S_{\bar{x}}$ and $S_{\bar{d}}$, will be discussed later.

The statistical analysis of the data from the "Central Composite Rotatable Design" in two X-variables is discussed below. The method of data analysis used is similar to that shown in Ref. 9.

Table VII below lists the nitrogen conversion obtained at each of the points in the design.

TABLE VII. EXPERIMENTAL DESIGN CONVERSION DATA

<u>Design Point</u>	<u>Percent Conversion</u>
1	90.80
1	90.90
1	89.55
1	91.25
1	91.95
2	87.85
3	83.75
4	85.50
5	87.15
6	87.80
7	84.25
8	84.85
9	86.35

Initially, this data was utilized to determine the second order fitted response surface in the coded scale. The resulting fitted response surface in the coded scale is shown below.

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2$$

or

$$\hat{y} = 90.89 - 0.5025x_1 + 1.240x_2 - 2.733x_1^2 - 2.200x_2^2 + 0.6125x_1x_2$$

where, \hat{y} = the estimated nitrogen conversion, percent

x_1 and x_2 = coded scale values of weight percent
nickel and tungsten, respectively

b_i and b_{ij} = the regression coefficients:

$i = 0, 1, 2$

$j = 1, 2$

The Analysis of Variance Table for the "Central Composite Rotatable Design" is shown below. An examination of this table leads to the following conclusions about the fitted response surface.

TABLE VIII. ANALYSIS OF VARIANCE: CENTRAL COMPOSITE ROTATABLE DESIGN

<u>Source of Variation</u>	<u>Degrees of Freedom</u>	<u>Sum of Squares</u>	<u>Mean Squares</u>	<u>F</u>
First-Order Terms	2	14.32	7.16	9.36
Second-Order Terms	3	78.02	26.01	34.00
Lack of Fit	3	0.90	0.30	0.39
Experimental Error	4	3.06	0.765	----
Total	12	96.30	-----	----

First, since the mean square for lack of fit is of the same order of magnitude as the experimental error mean square, a second order response surface appears to be adequate for describing the true response

surface. $F_{0.01}$ with 3 and 4 degrees of freedom is 16.69. Also, both the first and second order terms give significant mean squares. Therefore, all terms in the response surface equation should be retained.

The standard error of the various regression coefficients are:

$$\text{s.e. } (b_1) = \text{s.e. } (b_2) = s\sqrt{0.125} = 0.310$$

$$\text{s.e. } (b_{11}) = \text{s.e. } (b_{22}) = s\sqrt{0.125 + 0.01875} = 0.332$$

$$\text{s.e. } (b_{12}) = s\sqrt{0.25} = 0.438$$

An examination of the fitted surface indicated that the position of maximum \hat{y} is located at the position $x_1 = -0.06159$ and $x_2 = 0.27082$, in the coded scale. This corresponds to a catalyst with $x_1 = 6.78$ weight percent nickel and $x_2 = 17.92$ weight percent tungsten in the actual scale. This is the "optimum" catalyst composition for a catalyst of maximum hydrodenitrogenation activity. The estimated maximum \hat{y} from the fitted response surface is 91.07 percent nitrogen conversion. This is, of course, with the operating conditions utilized for the design tests.

In order to further interpret the data from the "Central Composite Rotatable Design" in two x-variables, an analysis was made of the resulting contour surface. In Figure 16A, some contours of equal response are plotted; i.e., plots of constant \hat{y} are shown. This Figure, page 160, should be consulted during the reading of the following discussion of the "Central Composite Rotatable Design" results.

The results obtained from the experimental design indicate that we can be at least 95 percent confident that the catalyst corresponding to the experimental design's center point is significantly more active than any of the other experimental design catalysts. That is, we can be at least 95 percent confident that the catalyst composition corresponding to that of the center point of the design ($x_1 = 7.00$; $x_2 = 16.00$) produces a more active catalyst than any of the other experimental design catalysts. The mean conversion obtained with this catalyst was 90.89 percent, ($S_d^t_{0.05,4} = 2.66$ and $90.89 - 2.66 = 88.23$). In fact, we can be at least 99 percent confident that this catalyst is significantly more active than all of the other catalysts in the design except the design point catalysts 2, 5, and 6. It would, therefore, appear that the most economical of the catalysts to produce of the four "best" catalyst compositions tested in the design is also the most active catalyst; i.e., the $x_1 = 7.00$ and $x_2 = 16.00$ composition catalyst. These same conclusions can be drawn about the predicted "optimum" catalyst in comparing it with all of the design's catalysts except the design center point catalyst.

As noted in Figure 16A, by the plotted contours of constant \hat{y} , the response surface is relatively flat over the range of x_1 and x_2 values studied. Also, it is noted that the range of variables tested produces a maximum. Since $S_d^t_{0.05,4} = 2.66$, the $\hat{y} = 88.41 = \hat{y}_{\max} - S_d^t_{0.05,4} = 91.07 - 2.66$ corresponds to the range of catalyst compositions which are

within the 95 percent confidence interval range of the "optimum" catalyst composition. Catalyst compositions within the $86.66 \hat{y}$ ellipse range are within the 99 percent confidence range of the "optimum" composition catalyst.

$$(\hat{y}_{\max} S_d^{t_{0.01,4}} = 86.66 = \hat{y})$$

As noted in Figure 16A, the predicted optimum conversion (91.07 percent) occurs at $x_1 = 6.78$ weight percent nickel and $x_2 = 17.92$ weight percent tungsten. This composition is quite near that of the catalyst at the center point of the design ($x_1 = 7.00$; $x_2 = 16.00$) and the mean conversion for the design center point catalyst (90.89 percent) was quite near the predicted optimum. For these reasons and the fact that this "Central Composite Rotatable Design" center point catalyst had been used to obtain data on the effect of the process variables, temperature and pressure, on the activity of the catalyst, a catalyst with optimum catalyst composition was not prepared and tested. This did not seem to be necessary in view of the fact that the design center point catalyst was nearly identical to the predicted optimum catalyst composition and its activity was also near that of the predicted optimum.

Using the $S_{\bar{d}}$ value obtained from an analysis of the design's results, $S_{\bar{d}} = 0.958$, it is noted that we can not even be 50 percent confident that the predicted optimum conversion at $x_1 = 6.78$ and $x_2 = 17.92$ is significantly different from the design center point mean conversion ($S_{\bar{d}}^{t_{0.5,4}} = 0.71$). For any point within the $\hat{y} = 90.36 = 91.07 - 0.71$

contour, Figure 16A, we are not more than 50 percent confident that the conversion obtained will be different from the conversion obtained with the predicted optimum composition catalyst. Therefore, as noted previously, it is felt that the design center point catalyst conversion is quite representative of the conversion that could be obtained with the predicted optimum catalyst. In essence, these results simply mean that the response surface is fairly flat around the predicted "optimum" composition.

Catalyst Evaluation (Comparison) Tests

Considering the results obtained from this analysis of the "Central Composite Rotatable Design" data, it was felt that the data obtained utilizing the center point of the designs catalyst was similar to what would be obtained with the "optimized" catalyst composition. Therefore, a few tests were conducted in order to facilitate an adequate comparison of the developed catalyst's activity with the commercial catalysts tested earlier. The results of this catalyst comparison study are summarized in Figures 17A and 18A. Figures 19A and 20A present the results of tests conducted in order to determine the effect of the process variables, temperature and L.H.S.V., on the developed catalyst activity. These Figures are discussed in detail below.

The catalyst comparison test results presented in Figures 17A and 18A clearly indicate the superiority of the nickel tungsten type catalyst on a silica-alumina support over the commercially available cobalt/nickel

molybdate hydrotreating catalysts for the hydrodenitrogenation of petroleum gas oils. Houdry "C" catalyst was the most active of the cobalt/nickel molybdate catalysts tested. It is also noted that the nickel tungsten type catalyst on an alumina support is not as active for hydrodenitrogenation as a similar catalyst on a silica-alumina support. The results presented in these figures also indicate that the developed "optimum" nickel tungsten sulfide catalyst is as active as Harshaw's hydrocracking, Ni-4401-E nickel in the reduced form, tungsten as the sulfide, catalyst. Harshaw's catalyst contains 6 percent nickel and 19 percent tungsten on a silica-alumina support which contains approximately 50 percent silica (SiO_2). The developed nickel tungsten sulfide catalysts contain approximately 7 percent nickel and 18 percent tungsten on a silica-alumina support which contains between 5 and 7 percent silica. This catalyst requires presulfiding to convert the metal oxides to the sulfide form, for a catalyst of maximum activity.

Figures 17A and 18A both indicate the increased catalyst activity resulting from the use of a silica alumina support instead of an alumina support. The increase in catalyst activity resulting from using nickel as a promoter on the tungsten catalyst is also noted in Figure 18A.

Effect of L.H.S.V. and Temperature on the Developed Catalyst Activity

The results presented in Figure 19A show the effect of temperature on the developed catalyst activity for hydrotreating petroleum gas oils. Over the 700 to 800°F range, at the 0.5 L.H.S.V. employed, the sulfur

removal was always greater than 95 percent. As expected, the sulfur conversion increased with increasing temperature at the constant L.H.S.V. employed. The heavy gas oil employed contained 0.824 weight percent sulfur. Over this same range of temperature, at 0.5 L.H.S.V., the nitrogen conversion decreased from 91 percent at 800°F to approximately 54 percent at 700°F. The results indicate that for a high degree of denitrogenation of high nitrogen content gas oils, temperatures greater than 750°F would probably be required even when employing the highly active nickel tungsten sulfide on a silica-alumina support catalyst at 0.5 L.H.S.V. and 1000 psig.

In Figure 20A the effect of L.H.S.V. on the developed catalyst hydrotreating activity is shown. The L.H.S.V. was varied from 0.25 to 2.0 and the temperature was held constant at 800°F. It is noted that the sulfur conversion was greater than 97 percent over the range of L.H.S.V. employed. As expected, the sulfur conversion decreased with increasing L.H.S.V. The nitrogen conversion decreased from 97.5 percent at the L.H.S.V. of 0.25 to 52.5 percent at a L.H.S.V. of 2.0. The results indicate that a L.H.S.V. of near 0.5 or less is needed in conjunction with the 800°F temperature to insure a high degree of nitrogen removal from high nitrogen content petroleum gas oil even when utilizing the highly active nickel tungsten type catalyst. As noted previously, all tests were conducted at 1000 psig and increasing the pressure would increase the nitrogen conversion.

As noted in Table VI-A, the effect of acid washing the product samples prior to analysis to remove nitrogen was investigated. This was done, primarily, during the Experimental Design portion of the research effort. It was noted that a dilute acid (3% HCl) wash could remove some of the nitrogen from the product samples. The higher the nitrogen content of the product, the more effective at removing the nitrogen was the dilute acid wash; i.e., a greater amount of nitrogen was removed from the product samples with the highest nitrogen content. In general, the samples were not acid washed prior to analysis.

SUMMARY AND CONCLUSIONS

In summary, the major conclusions obtained from the research work presented herein were:

- (1) That a properly prepared nickel tungsten catalyst on a silica-alumina support is more effective at removing nitrogen from high nitrogen content petroleum gas oils than the present commercially used cobalt/nickel molybdate catalysts.
- (2) Use of a silica-alumina catalyst support containing 5 to 7 percent silica (SiO_2) by weight results in a more active catalyst than a similar catalyst on an alumina support.
- (3) Proper sulfiding of the catalyst prior to use can result in a more effective (active) catalyst; i.e., the catalyst is more active when the metals are in their sulfide form rather than the oxide form. Catalyst presulfiding is recommended for maximum catalyst activity.
- (4) For maximum catalyst hydrodenitrogenation activity, a catalyst containing approximately 7 percent by weight nickel and 18 percent by weight tungsten is required. It was noted, however, that the response surface is relatively flat near the point of "optimum" catalyst composition.

- (5) That of the conventional hydrotreating catalyst promoters (nickel, cobalt, and molybdenum), nickel is by far the most effective promoter for the tungsten type hydrodesulfurization catalyst.
- (6) The developed nickel tungsten catalyst is a very active hydrodenitrogenation catalyst. Sulfur is removed much easier than nitrogen even though it is present in a much higher concentration.
- (7) Although a complete analysis of the product was not made at all test conditions, hydrocracking can be kept below a level which will result in "excessive" coking of the catalyst; i.e., high nitrogen removal can be obtained without causing "excessive" catalyst deactivation due to catalyst coking during hydrotreating.
- (8) As expected, the developed catalyst's hydrodenitrogenation activity decreased with increasing L.H.S.V. and decreasing temperature. When hydrotreating the Santa Maria high nitrogen content gas oil at 1000 psig and 5000 SCF H₂ per bbl, a temperature of 750°F or greater was required for high (>80%) nitrogen removal at a L.H.S.V. of 0.5 and a 0.7 or less L.H.S.V. was required at the 800°F temperature level.

- (9) That the developed catalyst is superior to currently available, commercially used hydrodenitrogenation catalysts. It is rugged, long-lived, and operated at temperatures and pressures that are moderate and economical to obtain.
- (10) In view of the above results, the research objectives were realized.

RECOMMENDATIONS FOR FURTHER WORK

The results of the research work presented herein and that presented in Reference 20 indicate that improved catalytic processes can be developed for more effective removal of nitrogen from petroleum gas oils. Although many possibilities exist for further work on the removal of nitrogen from petroleum fractions or their potential substitute oils, it is believed that the most fruitful would be the following:

- (1) Investigations into the possible use of other metals as catalysts of greater activity than those presently used.
- (2) Investigations into other possible methods (processes) by which the nitrogen may be removed from the oil; i.e., investigations of methods for the removal of the nitrogen by means other than hydro-treating the oil to obtain a hydrocarbon and ammonia as the products.
- (3) Investigations into other possible catalyst supports and preparation techniques for the metal catalysts; i.e., evaluate other catalyst supports such as molecular sieves, unsupported, etc., or other catalyst preparation variables in order to increase the catalyst activity.

As noted in the INTRODUCTION section of this thesis, the results of

this research should be of considerable practical value since the nitrogen compounds in petroleum and its potential oil substitutes are similar in nature. Possibly the catalyst developed herein should be evaluated for hydrotreating the various potential petroleum substitute oils such as shale oil, products from coal hydrogenation, or oil from the tar sands in Canada.

An investigation into the effect of feedstock variables on the nickel tungsten catalyst's hydrodenitrogenation activity also seems justified. Such a study should include a complete analysis of both the feedstock and the product streams, nitrogen analysis, sulfur analysis, ASTM distillation, etc.

APPENDIX

TABLE I-A. FEEDSTOCK PROPERTIES

Feedstock Identification Number	1	2	3	4	5
Supplier of Feedstock	California Research Corporation	California Research Corporation	California Research Corporation	Richfield Oil Corporation	Shell Development Company
Weight Percent Nitrogen (Total)	0.238	0.181	0.319	0.256	0.335
Weight Percent Sulfur (Total)	0.74*	0.58	0.824	1.07*	1.18*
*Gravity, °API	21.9	23.5	----	21.0	22.9
*Boiling Range					
IBP	543°F	540°F	----	495°F	----
10%	651	612	----	633	640°F
50%	714	675	----	746	770
90%	793	750	----	870	920

-76-

*Properties supplied by supplier of feedstock. (Boiling range determined by ASTM Distillation D-1160, with temperatures corrected to 760 mm.)

TABLE II-A. COMMERCIAL CATALYST PROPERTIES*

Catalyst Manufacturer and Identifi- cation Symbol	Weight Percent Ni or NiO	Weight Percent Co or CoO	Weight Percent Primary Metal; Mo, MoO ₃ , or W	Surface Area (M ² /g)	Pore Vol. (cc/g)	Apparent Bulk Density (#/ft ³)	Ave. Pore Dia. (A°)	Support Type and Size
Peter Spence & Sons, Ltd. (P.S.)	----	2.5 (CoO)	14.0 (MoO ₃)	----	----	----	----	1/8" x 1/8" al- umina pellets
Houdry Pro- cess & Chem. Co. (Houdry "C")	----	3.0 (CoO)	15.0 (MoO ₃)	310 to 340	0.45	53	55	1/8" al- umina ex- trusions
American Cyanamid Co. (Aero HDS-3)	3.1 (NiO)	----	15.0 (MoO ₃)	200	0.60	35	----	1/8" al- umina ex- trusions
American Cyanamid Co. (Aero HDS-2)	----	3.0 (CoO)	15.0 (MoO ₃)	260	0.55	43	----	1/8" al- umina ex- trusions
Filtrol Corp. (FG 500-8)	2.25 , (Ni)	1.25 (Co)	11.0 (Mo)	>300	0.44	46	50	1/8" al- umina ex- trusions
Filtrol Corp. (FG 475-8)	----	2.8 (CoO)	15.0 (MoO ₃)	>300	0.43	45	50	1/8" al- umina ex- trusions
Girdler Catalysts (G-35B)	--	3.5 (CoO)	10.0 (MoO ₃)	210	0.27	60	55	3/16" x 1/8" al- umina tablets

*Properties obtained from the manufacturer.

1051

TABLE II-A (continued) *

Catalyst Manufacturer and Identifi- cation Symbol	Weight Percent Ni or NiO	Weight Percent Co or CoO	Weight Percent Primary Metal; Mo. MoO ₃ , or W	Surface Area (M ² /g)	Pore Vol. (cc/g)	Apparent Bulk Density (#/ft ³)	Ave. Pore Dia. (A°)	Support Type and Size
Davison Chem. (Nicomo 12)	0.3 (Ni)	1.9 (Co)	10.0 (Mo)	200	0.35	41	----	1/8" al- umina ex- trusions
Nalco Chem. Co. (Nalcomo 471)	----	3.5 (Co)	12.5 (MoO ₃)	270	0.48	40	71	1/8" al- umina ex- trusions
Harshaw Chem. (Ni-4401-E)	6.0 (Ni)	----	19.0 (W)	212	0.39	59	----	1/8" silica alumina ex- trusions
Harshaw Chem. (Ni-4403-E)	6.0 (Ni)	----	19.0 (W)	140	0.48	50	----	1/8" al- umina ex- trusions

*Properties obtained from the manufacturer.

TABLE III-A. CATALYST SUPPORT PROPERTIES¹

Manufacturer	Identification Number	Support Type and Size ²	Surface Area M ² /g	Pore Volume cc/g	Apparent Bulk Density #/ft ³	Pore Dia. °A ³
Harshaw Chem.	Al-0104-T	1/8" alumina tablets	80 to 100	0.28 to 0.33	44 to 58	----
Harshaw Chem.	Al-1404-T	1/8" alumina tablets	180 to 200	0.42 to 0.51	47 to 55	----
*Harshaw Chem.	Al-1602-T	1/8" silica-alumina tablets	210 to 240	0.48	52	----
*Harshaw Chem.	Al-1706-E	1/8" alumina extrusions	207	0.82	35	----
*Harshaw Chem.	Al-1802-E	1/8" silica-alumina extrusions	277	0.91	33	----
Harshaw Chem.	Al-1906-E	1/8" alumina extrusions	181	0.56	42	----
*Chemical Products Division Chemetron Corp. Girdler Catalysts	T-126	1/8" by 3/16" alumina tablets	200 to 250	0.30	----	----

1. Properties supplied by manufacturer.

2. The silica-alumina supports contained approximately six percent silica (SiO₂).

* Supports that were tested.

3. °A = Angstroms.

TABLE III-A (continued)¹

Manufacturer	Identification Number	Support Type and Size ²	Surface Area M ² /g	Pore Volume cc/g	Apparent Bulk Density	Pore Dia. °A ³
*Nalco Chem.	64-2542	1/16" alumina extrusions	250	0.60	33	96
Aluminum Co. of America (Alcoa)	H-51	8 to 14 mesh silica-alumina	350	0.50	52 to 59	60
Aluminum Co. of America (Alcoa)	F-110	1/8" alumina balls	180 to 280	0.38	55	50
Aluminum Co. of America (Alcoa)	H-151	1/8" silica-alumina balls	350	0.30	52 to 55	50
Kaiser Chem.	KA-101	1/8" alumina tablets	360	0.57	45	64

1. Properties supplied by manufacturer.

2. The silica-alumina supports contained approximately six percent silica (SiO₂).

* Supports that were tested.

3. °A = Angstroms.

TABLE IV-A. PROPERTIES OF THE PREPARED CATALYSTS

Catalyst Identification Symbol	Weight Percent Promoter ¹	Weight Percent Tungsten	Catalyst Support Used ²
P-1	0.0	14.5	T-126
* P-2	5.5	13.8	T-126
P-3	4.7	14.1	T-126
P-4	12.9	0.0	T-126
P-5	0.0	20.2	64-2542
P-6	8.7 (Cobalt)	17.8	64-2542
P-7	9.1 (Molyb-	17.0	64-2542
P-8	8.4 denum)	18.0	64-2542
P-9	6.0	14.8	64-2542
P-10	6.0	15.5	64-2542
P-11	5.9	15.5	A1-1802-E
P-12	5.1	12.5	A1-1602-T
P-13	4.7	16.4	A1-1602-T
P-14	5.3	15.7	A1-1706-E
P-15	8.0	17.5	64-2542
P-16	6.2	15.1	A1-1602-T
ED-1	7.5	15.1	A1-1802-E
ED-2	10.2	23.1	A1-1802-E
ED-3	10.8	9.0	A1-1802-E
ED-4	3.5	9.0	A1-1802-E
ED-5	3.5	23.0	A1-1802-E
ED-6	6.8	25.8	A1-1802-E
ED-7	11.2	15.9	A1-1802-E
ED-8	7.0	6.0	A1-1802-E
ED-9	2.5	16.0	A1-1802-E

¹ Unless otherwise noted, the promoter was nickel.

² See Table III-A on the previous pages.

* Nickel impregnated first. (For all other catalysts the tungsten was impregnated first.)

TABLE V-A. TABULAR SUMMARY OF RUN NUMBERS, OPERATING CONDITIONS, AND RUN OBJECTIVE(S)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
1	Houdry "C"	1	Hydrogen flow rate = 8,000 SCF/bbl. Catalyst not presulfided.	<u>Exploratory test.</u> To determine run length necessary to ensure complete lineout. To determine reasonable operating conditions for catalyst comparison tests.
2	Houdry "C"	1	Same as Run 1.	To determine experimental error (precision).
3	Houdry "C"	1	Same as Run 1.	To determine experimental error (precision).

¹ See Table II-A or IV-A for identification of the catalysts from the symbols given below.

² See Table I-A for feedstock properties.

³ Only conditions other than the standard operating conditions will be noted below. The standard operating conditions were:

- (a) Operating pressure = 1000 psig.
- (b) Operating temperature = 800°F.
- (c) Liquid Hourly Space Velocity = L.H.S.V. = 0.5 ml of oil/hr-ml of catalyst.
- (d) Hydrogen flow rate = 5000 SCF/bbl of oil.
- (e) 120 ml catalyst charge
- (f) Catalyst presulfided by passing a 20 percent hydrogen sulfide - 80 percent hydrogen (by volume) gaseous mixture over the catalyst, at 650°F, at the rate of 2 standard cubic feet of gaseous mixture per hour. Sulfur equal to one-half of the weight of the catalyst was passed over the catalyst. (The catalyst was allowed to cool to room temperature before starting the test run.)

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
4	Houdry "C"	1	Hydrogen flow rate 8,000 SCF/bbl.	To determine the effect that sulfiding the catalyst has on its hydrodenitrogenation activity.
5	Houdry "C"	1	Same as Run 4.	To determine experimental error (precision).
6	Houdry "C"	1	Hydrogen flow rate = 16,000 SCF/bbl.	Used with Run 4 to determine the hydrogen flow rate necessary to assure that the hydrogen flow rate does not limit the nitrogen-removing ability of the catalyst.
7	Houdry "C"	1	Hydrogen flow rate = 2,500 SCF/bbl.	"
8	Houdry "C"	1	Hydrogen flow rate = 1,000 SCF/bbl.	"
9	Houdry "C"	1	Hydrogen flow rate = 5,000 SCF/bbl.	"
10	Houdry "C"	1	90 ml catalyst charge	Used with Run 9 to determine that film diffusion was not controlling the reaction rate, and thereby the nitrogen conversion, at the test conditions being employed.
11	Houdry "C"	1	60 ml catalyst charge	
12	Houdry "C"	1	L.H.S.V. = 1.0	
13	Houdry "C"	1	60 ml catalyst charge L.H.S.V. = 1.0	"
14	Houdry "C"	1	30 ml catalyst charge L.H.S.V. = 1.0	"

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
15	P.S.	1	"Standard"	
16	Houdry "C"	1	Temperature = 750°F	
17	P.S.	1	Same as Run 16.	CATALYST
18	FG 500-8	1	Same as Run 16	
19	FG 475-8	1	Same as Run 16.	ACTIVITY
20	Nicomo 12	1	Same as Run 16.	
21	Aero HDS-3	1	Same as Run 16.	COMPARISON
22	Aero HDS-2	1	Same as Run 16.	
23	Nalcomo 471	1	Same as Run 16.	TESTS
24	G-35B	1	Same as Run 16.	
25	FG 500-8	1	"Standard"	"
26	Aero HDS-3	1	"Standard"	"
27	FG 475-8	1	"Standard"	"
*28-A	FG 500-8	1	L.H.S.V. = 1.0	To determine the effect of space velocity and temperature on the nitrogen removing capability of commercial nickel/cobalt molybdate hydrotreating catalysts.
*28-B	FG 500-8		L.H.S.V. = 2.0	
*29-A	FG 500-8	1	Temperature = 750°F L.H.S.V. = 1.0	
*29-B	FG 500-8	1	Temperature = 750°F L.H.S.V. = 2.0	
30	FG 500-8	1	Temperature = 700°F	"
*31-A	FG 500-8	1	Temperature = 700°F L.H.S.V. = 1.0	"
*31-B	FG 500-8	1	Temperature = 700°F L.H.S.V. = 2.0	"

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
*32-A	FG 500-8	1	60 ml cat. charge L.H.S.V. = 5.0	To determine the effect of space velocity and temperature on the nitrogen-removing capability of commercial nickel/cobalt molybdate hydrotreating catalysts.
*32-B	FG 500-8	1	60 ml cat. charge Temp. = 750°F L.H.S.V. = 5.0	
33	FG 500-8	1	60 ml cat. charge Temp. = 700°F L.H.S.V. = 5.0	"
34	Houdry "C"	1	Temperature = 750°F L.H.S.V. = 1.0	"
35	P.S.	1	Temperature = 750°F L.H.S.V. = 1.0	"
36	P.S.	1	Temperature = 800°F L.H.S.V. = 1.0	"

* Note that some runs have more than one set of operating conditions per run.

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
**37 ⁴	Ni-4401-E	2, 4, and 5 (Feedstocks 4 & 5 were used for only approx. 2 days each)	Catalyst not presulfided. Received in sulfided form. Temp. 800°F for first 62.5 days except for brief 12-hr period at 750°F. Temp. 820°F for last 27.5 days.	To evaluate Nickel Tungsten type catalysts for hydrodenitrogenation. To demonstrate catalyst life capability of the tungsten type catalysts for hydrodenitrogenation of high nitrogen content petroleum feedstocks.
38 ⁴	Ni-4401-E	2	"Standard"	To determine experimental error (precision). To obtain an analysis of the effluent gas from the reactor.
39 ⁴	Ni-4401-E	2	"Standard"	"

** Extended 90-day test run.

* A "P" after a run number indicates that the run was a preliminary catalyst preparation test run. That is, it was used to obtain information on the best method of preparing a tungsten hydrotreating catalyst. The "best method" being the method that yields the most active catalyst.

⁴ Catalyst received in sulfided form from manufacturer. (Presulfiding not required.)

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
40 ⁴	Ni-4403-E	2	"Standard"	Catalyst Activity Comparison Test.
41 ⁴	Ni-4401-E	3	"Standard"	Catalyst Activity Comparison Tests.
42	Hourdry "C"	3	"Standard"	"
*43-P	P-1	3	"Standard"	To determine if an active tungsten type catalyst could be prepared in the laboratory.
44-P	P-4	3	"Standard"	To determine the activity of a nickel catalyst for hydrodenitrogenation.
45-P	P-2	3	"Standard"	To determine if the order of metal impregnation affects the catalyst's activity. To evaluate T-126 catalyst support.
46-P	P-3	3	"Standard"	"
47-P	64-2542 (pellets only)	3	"Standard"	Catalyst Activity Comparison Test.
48-P	P-5	3	"Standard"	To determine the activity of an unpromoted tungsten catalyst.
49-P	P-6	3	"Standard"	To evaluate cobalt as a promoter.

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
50-P	P-7	3	"Standard"	To evaluate molybdenum as a promoter.
51-P	P-8	3	"Standard"	To evaluate nickel as a promoter.
52-P	P-9	3	"Standard"	To evaluate 64-2542 catalyst support. To determine if the catalyst preparation is reasonably repeatable. To determine test run repeatability/ (experimental error).
53-P-1	P-10	3	"Standard"	"
53-P-2	P-10	3	"Standard"	"
54-P	P-15	3	"Standard"	To determine the effect that sulfiding temperature and the amount of 80 percent hydrogen-20 percent hydrogen sulfide (by volume) that is passed over the catalyst has on its activity.
55-P	P-15	3	Catalyst pre-sulfided at 350°F.	"

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
56-P	P-15	3	Catalyst pre-sulfided by passing sulfur equal to 5 times the weight of the catalyst over the catalyst.	To determine the effect that sulfiding temperature and the amount of 80 percent hydrogen-20 percent hydrogen sulfide (by volume) that is passed over the catalyst has on its activity.
57-P	P-15	3	No catalyst pre-treatment. (Metals in oxide form.)	Same as Runs 54-P, 55-P, 56-P.
58-P	P-15	3	Catalyst Presulfided with a solution of CS ₂ in cyclohexane.	Same as 59-P.

* During these pretreatments the reactor was run the same as during the test run except that the pretreating solution was fed to the reactor, and passed over the catalyst, instead of the feedstock (gas oil). This condition was maintained for approximately 24 hours before the feedstock was fed to the reactor.

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
59-P	P-15	3	Catalyst pretreated with a solution of pyridine in cyclohexane.	*To determine if the catalysts can be effectively sulfided with other than the gaseous H ₂ S-H ₂ mixture. (A 5 percent by wt. sulfur solution made by diluting CS ₂ in cyclohexane was used.) To determine the effect that pretreating the catalyst with a nitrogen-containing solution prior to use has on its hydrodenitrogenation activity. (A 5 percent by weight nitrogen solution made by diluting pyridine in cyclohexane was used.)
60-P	P-11	3	"Standard"	To evaluate Al-1802E catalyst support.

* During this pretreatment the reactor was run the same as during the test run except that the pretreating solution was fed to the reactor and passed over the catalyst instead of the feedstock (gas oil). This condition was maintained for approximately 24 hours before the feedstock was fed to the reactor.

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
61-P	P-12	3	"Standard"	To evaluate Al-1602E catalyst support.
62-P	P-13	3	"Standard"	"
63-P	P-14	3	"Standard"	To evaluate Al-1706E catalyst support.
64-P	P-16	3	"Standard"	**To determine the best manner in which to start the test runs.
65-P	P-16	3	Run started with catalyst at 650°F when contacted with the initial feedstock flow.	"
66-P	P-16	3	Catalyst subjected to reducing atmosphere, hydrogen, at 650°F, after sulfiding.	"

** The differences in test run startup are discussed in detail on page 66.

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
67	Houdry "C"	3	"Standard"	Catalyst Activity Comparison Test.
*68-ED	ED-9	3	"Standard"	To obtain experimental design data.
69-ED	ED-8	3	"Standard"	"
70	P-16	3	L.H.S.V. = 0.25	To determine the effect of L.H.S.V. on nitrogen conversion.
71-ED-1	ED-1	3	"Standard"	To obtain experimental design data.
71-2	ED-1	3	L.H.S.V. = 1.0	To determine the effect of L.H.S.V. on nitrogen conversion.
72-ED	ED-2	3	"Standard"	To obtain experimental design data.

* An "ED" after a run number indicates that it was one of the runs performed for the completion of the experimental design. (The experimental design was used to determine the optimum weight percent of nickel and tungsten that should be impregnated onto the support to give a catalyst of maximum activity.)

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
73-ED	ED-6	3	"Standard"	To obtain experimental design data.
74-ED	ED-4	3	"Standard"	To obtain experimental design data.
75-ED-1	ED-1	3	"Standard"	To obtain experimental design data.
75-2	ED-1	3	Temp. = 700°F.	To determine the effect of temperature on nitrogen conversion.
75-3	ED-1	3	Temp. = 725°F.	"
76	Houdry "C"	2	"Standard"	Catalyst Activity Comparison Test.
77-ED	ED-3	3	"Standard"	To obtain experimental design data.
78-ED-1	ED-1	3	"Standard"	"
78-2	ED-1	3	L.H.S.V. = 2.0	To determine the effect of L.H.S.V. on nitrogen conversion.
79-ED	ED-5	3	"Standard"	To obtain experimental design data.
80-ED	ED-7	3	"Standard"	"
81-ED-1	ED-1	3	"Standard"	"

TABLE V-A (continued)

Run Number	Catalyst Used ¹ (Identification Symbol)	Feedstock ² (Identification Number)	Operating Conditions ³	Run Objective(s)
81-2	ED-1	3	Temp. = 750°F	To determine the effect of temperature on nitrogen conversion.
82-ED-1	ED-1	3	"Standard"	To obtain experimental design data.
82-2	ED-1	3	L.H.S.V. = 1.5	To determine the effect of L.H.S.V. on nitrogen conversion.
83	ED-1	2	"Standard"	Catalyst Activity Comparison Test.
84-1	ED-1	3	Hydrogen flow-rate = 2,500 SCF/bbl.	To check that film diffusion was not controlling the reaction rate, and thereby the nitrogen conversion.
84-2	ED-1	3	H ₂ Flow rate =	"
85	ED-1	3	10,000 SCF/bbl. L.H.S.V. = 0.25	To determine the effect of L.H.S.V. on the nitrogen conversion.

TABLE VI-A. EXPERIMENTAL NITROGEN AND SULFUR CONVERSION DATA

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
1	4.0	76.1	74.4
	6.0	72.3	72.7
	8.0	77.7	----
	10.0	77.4	----
	12.0	76.9	76.9
	14.0	76.9	76.5
	16.0	77.7	----
	19.5	79.8	78.2
	23.5	78.2	78.2
	27.0	77.5	77.5
	31.0	80.2	79.0
	38.5	80.3	79.9
	41.0	80.3	79.5
	44.0	78.6	78.2
	48.5	81.1	79.4
----		Average ⁴ = 78.5	

¹ See Table V-A for run conditions.

² An 'S' in parenthesis after a percent-conversion figure means that it is percent sulfur conversion.

A 'WW' in parenthesis after a conversion figure means that the sample was water washed prior to the analysis.

An 'AW' in parenthesis after a conversion figure means that the sample was acid washed prior to analysis. An acid wash was always followed by a water wash. After washing, the samples were filtered. (Acid washing was done with a 3 percent, by weight, HCl solution.)

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
2	4.0	72.6	73.5
	6.0	74.6	76.3
	8.0	78.5	77.5
	11.0	78.9	78.9
	13.0	79.8	79.3
	18.0	79.7	79.3
	26.0	80.3	81.1
	30.0	80.6	80.3
	33.0	78.9	79.4
	36.0	80.4	79.4
	41.5	80.2	80.2
	----	Average = 79.9	
3	7.0	76.5	75.2
	11.0	76.7	77.2
	14.0	78.2	77.4
	18.0	80.7	78.6
	22.0	78.7	79.3

³ The column marked 'A-1' denotes the first analysis of the sample. Column A-2 contains the duplicate analysis of the sample.

⁴ Mean conversion for the test; i.e., the mean of the analyses after lineout. This is the mean conversion of the samples taken after 12 hours on stream.

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
3	30.5	80.7	78.3
	36.0	79.4	80.3
	44.0	79.8	79.8
	50.0	80.2	79.4
	-----	Average = 79.3	
4	3.0	91.8	91.8
	5.0	88.8	89.3
	7.5	88.0	87.2
	9.5	86.3	85.9
	11.0	86.7	86.7
	13.0	86.3	85.8
	15.0	85.5	84.7
	20.0	86.3	86.3
	25.0	84.3	83.4
	30.0	84.7	84.7
	35.0	84.7	84.7
	40.0	83.4	83.4
	45.0	83.6	84.4
50.0	83.8	84.3	
-----	Average = 84.7		
5	3.0	94.7	93.2
	5.5	91.0	91.0
	7.0	90.2	90.2
	11.0	87.7	88.0
	13.0	86.8	-----
	15.0	84.6	85.3

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
5	17.5	86.6	85.2
	23.0	85.8	----
	28.0	83.4	85.2
	33.5	85.5	86.6
	----	Average = 85.5	
6	8.5	86.7	87.5
	12.0	86.2	85.0
	15.0	87.2	----
	18.0	87.4	86.5
	28.0	86.7	86.7
----	Average = 86.5		
7	12.0	81.2	82.4
	15.0	82.0	80.7
	18.5	81.0	81.5
	21.0	81.5	81.5
	26.0	81.0	82.5
	34.0	81.6	81.2
----	Average = 81.5		
8	13.5	79.2	79.2
	17.0	78.7	75.1
	25.0	78.3	77.4
	36.0	78.6	79.5
	40.0	77.7	78.5
----	Average = 78.2		

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
9	15.0	85.6	84.5
	19.0	83.5	84.4
	25.0	84.2	84.4
	32.0	83.8	85.2
	----	Average = 84.4	
10	12.0	87.5	86.0
	16.0	84.0	86.2
	26.0	86.6	85.8
	36.0	88.0	86.7
	42.5	85.5	85.9
----	Average = 86.2		
11	13.0	84.3	83.0
	15.0	84.2	85.2
	21.0	83.0	----
	29.0	82.7	83.8
----	Average = 83.7		
12	12.0	62.2	63.0
	14.0	62.1	61.8
	16.0	62.9	60.9
	20.0	61.5	62.4
	28.5	62.0	61.2
----	Average = 62.0		

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
13	9.5	65.1	64.7
	13.0	62.2	62.6
	17.0	64.7	63.5
	24.0	62.3	----
	30.0	63.9	62.8
	----	Average = 63.1	
14	11.0	58.6	----
	16.5	58.2	58.2
	19.0	55.7	56.4
	22.0	58.2	58.7
	30.0	57.0	----
	----	Average = 57.6	
15	12.0	68.7	68.4
	18.0	65.7	67.0
	24.0	66.0	64.0
	29.0	64.7	63.5
	35.5	66.2	65.9
	----	Average = 66.0	
16	12.5	67.0	65.5
	17.0	66.6	66.6
	25.0	66.1	65.6
	28.0	67.0	68.0
	----	Average = 66.5	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
17	13.0	57.9	56.7
	17.5	58.5	58.5
	25.5	57.9	----
	34.0	58.9	57.7
	----	Average = 57.9	
18	12.0	45.8	47.6
	17.0	46.6	46.3
	35.0	46.0	46.0
	39.5	46.6	45.1
	----	Average = 46.2	
19	15.0	38.3	38.6
	21.0	37.1	36.5
	30.5	37.1	37.1
	----	Average = 37.4	
20	14.0	66.7	65.5
	22.5	67.7	----
	27.0	66.2	65.6
	38.0	65.7	66.9
	----	Average = 66.4	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
21	12.0	68.0	68.3
	26.0	65.7	65.9
	30.0	65.3	67.1
	36.5	65.7	----
	----	Average = 66.6	
22	12.0	56.3	56.9
	16.0	55.1	53.8
	22.0	54.7	55.0
	32.0	53.9	54.3
	----	Average = 55.0	
23	12.0	62.9	64.4
	17.5	60.7	60.1
	22.0	61.7	62.1
	26.0	59.2	----
	30.0	60.3	59.7
----	Average = 61.2		
24	12.0	55.5	56.4
	18.0	53.9	53.5
	26.0	55.5	56.4
	38.0	54.2	54.7
	----	Average = 55.0	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
25	13.0	68.4	68.0
	17.5	68.7	67.4
	26.5	67.4	66.8
	28.0	68.1	----
	40.0	67.7	66.4
	----	Average = 67.7	
26	12.0	85.4	85.1
	17.5	86.4	84.5
	24.5	82.9	82.6
	38.0	84.1	85.1
	----	Average = 84.5	
27	12.5	50.7	51.6
	18.0	51.0	51.0
	26.0	48.7	49.6
	33.5	49.4	48.0
	----	Average = 50.0	
28-A	8.0	55.2	56.4
	15.0	56.0	54.7
	20.0	55.0	55.5
	28.5	55.5	55.5
	32.0	54.8	56.6
	----	Average = 55.4	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
28-B	40.0	45.0	44.2
	46.5	43.3	42.9
	52.0	45.8	44.1
	----	Average = 44.2	
29-A	5.0	37.3	37.3
	12.0	36.7	33.2
	16.5	36.4	35.5
	20.0	36.7	37.5
	28.0	35.6	36.7
----	Average = 36.1		
29-B	36.0	25.6	24.5
	40.0	23.5	24.2
	46.0	23.8	25.2
----	Average = 24.4		
30	10.0	33.0	32.6
	15.0	30.1	30.5
	19.0	32.6	31.4
	25.0	30.2	31.8
	37.5	30.7	----
----	Average = 31.0		
31-A	7.0	18.3	19.1
	12.0	18.2	17.9
	18.0	19.0	17.0

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
31-A	26.0	17.6	18.5
	30.0	18.1	17.3
	----	Average = 17.9	
31-B	38.0	8.5	8.8
	44.0	7.3	6.7
	50.0	7.3	7.3
----	Average = 7.6		
32-A	5.5	25.4	26.7
	10.0	24.5	24.5
	15.0	23.1	23.1
	21.0	21.5	21.8
	33.0	21.8	20.7
----	Average = 22.0		
32-B	40.0	15.0	14.3
	45.0	14.1	13.5
	50.0	13.5	13.5
	58.0	14.5	13.8
----	Average = 14.1		
33	8.0	5.4	4.8
	13.0	3.2	3.5
	20.0	3.0	2.7

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
33	25.0	2.3	2.1
	30.0	2.5	2.7
	----	Average = 2.8	
34	8.0	49.1	48.7
	12.0	46.2	46.6
	14.0	48.7	47.5
	20.0	46.3	----
	30.0	47.9	46.8
----	Average = 47.1		
35	8.0	45.2	46.5
	12.0	44.7	44.0
	16.0	45.7	----
	20.0	45.9	45.5
	24.5	45.2	----
	29.0	44.6	----
----	Average = 45.1		
36	15.0	56.0	54.7
	21.0	55.9	56.9
	25.5	54.7	----
	28.0	54.4	55.5
----	Average = 55.4		

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
37	7.0	99.4	97.8
	16.5	97.8	98.9
	24.0	98.5	98.9
	36.0	96.7	96.2
	43.0	97.8	97.8
	53.0	97.2	97.2
	60.0	96.7	96.7
	-----	Average = 97.5	
	60.5	Switched from feed- stock #2 to feed- stock #4.	
	67.0	90.5	-----
	75.0	88.3	87.2
	87.5	90.2	88.7
	100.5	88.2	88.2
	110.0	88.2	88.6
	110.5	Switched from feed- stock #4 back to feedstock #2.	
	119.0	90.8	-----
	122.0	91.1	90.1
	123.0	Reduced temperature to 750°F.	
	127.0	77.3	81.1
	132.0	78.5	77.8
	134.0	Raised temperature back to 800°F.	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
37	143.0	93.9	91.7
	145.0	92.0	92.0
	146.0	Switched from feedstock #2 to feedstock #5.	
	158.0	82.6	82.1
	171.0	81.8	-----
	187.0	82.2	-----
	206.0	80.9	81.5
	207.0	Switched from feedstock #5 back to feedstock #2	
	216.0	88.4	89.5
	216.0	90.0(WW)	90.0(WW)
	276.0	89.7	-----
	327.0	89.5	88.4
	375.0	88.5	88.5
	448.0	87.3	-----
	472.0	86.3	86.3
	495.0	86.1	86.0
	590.0	86.7	86.1
	590.0	87.2(WW)	87.2(WW)
	615.0	87.2	87.2
	615.0	86.7(WW)	87.2(WW)
737.0	86.2	86.7	
737.0	85.2(WW)	85.2	
788.0	82.0	83.0	
832.0	83.5	83.8	
884.0	82.0	82.5	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
37	1094.0	79.6	78.4
	1190.0	77.4	76.3
	1214.0	77.9	----
	1335.0	74.0	74.4
	1485.0	74.7	----
	1499.0	Raised temperature to 820°F.	
	1509.0	85.2	----
	1527.0	85.5	----
	1551.0	84.4	83.4
	1622.0	80.0	80.0
	1701.0	78.5	78.7
	1725.0	78.1	78.7
	1840.0	77.9	79.5
	1865.0	76.0	----
	1966.0	78.7	----
	2125.0	74.4	----
2156.0	74.6	74.1	
38	26.0	98.2	98.7
	52.0	97.0	95.7
	80.0	96.5	96.5
	-----	Average = 97.1	
39	17.0	98.4	99.0
	22.0	98.9	98.4
	54.0	97.7	96.9
	66.0	96.5	97.2
		Average = 97.8	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
40.	15.0	90.7	91.8
	20.0	90.3	91.8
	26.0	91.5	90.8
	38.0	90.8	90.8
	-----	Average = 91.0	
41.	8.0	94.6	95.4
	16.5	92.1	-----
	27.0	92.5	91.9
	40.5	92.7	92.9
	48.0	91.7	-----
-----	Average = 92.2		
42	13.5	81.4	-----
	24.0	79.5	-----
	30.0	78.9	-----
	37.5	80.2	-----
-----	Average = 79.8		
43-P	10.0	75.8	75.5
	15.0	74.9	-----
	24.0	74.3	-----
	39.0	73.9	-----
	47.5	75.7	-----
-----	Average = 74.7		

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
44-P	8.5	65.8	----
	16.5	52.0	----
	24.0	52.3	----
	44.0	50.0	----
	-----	Average = 51.4	
45-P	9.0	87.8	----
	25.0	80.4	----
	31.0	80.3	----
	36.0	79.0	80.2
	-----	Average = 80.1	
46-P	7.0	90.0	89.0
	17.0	82.7	82.7
	20.0	83.4	----
	27.5	(Sample Lost)	
	46.0	81.6	----
	-----	Average = 82.6	
47-P	14.0	4.7	----
	22.0	3.5	----
	34.0	3.0	----
	-----	Average = 3.7	

TABLE VI-A (continued)

<u>Run Number</u> ¹	<u>Hours on Stream</u>	<u>Percent Conversion</u> ²	
		<u>A-1</u> ³	<u>A-2</u> ³
48-P	13.0	68.3	----
	20.0	70.4	----
	39.5	67.0	----
	47.0	66.3	----
	59.0	67.2	----
	----	Average =	67.8
49-P	5.5	78.0	----
	23.0	71.4	----
	26.0	72.7	----
	30.5	69.4	----
	34.0	69.7	----
	----	Average =	70.8
50-P	9.0	75.6	----
	15.0	71.7	----
	29.0	69.6	----
	54.0	69.0	----
	----	Average =	70.1
51-P	4.5	87.1	----
	15.5	80.3	----
	22.0	82.1	----
	29.0	79.0	----
	----	Average =	80.5

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
52-P	21.0	80.6	----
	31.5	80.0	----
	36.0	79.4	----
	----	Average = 80.0	
53-P-1	6.0	87.2	----
	21.0	80.7	81.9
	28.0	79.5	80.8
	47.0	78.4	----
	51.0	79.8	79.8
	----	Average = 79.9	
53-P-2	9.0	84.0	----
	20.0	80.8	----
	27.0	80.0	----
	48.0	79.9	----
	----	Average = 80.2	
54-P	4.0	86.4	
	15.0	79.2	----
	22.0	80.7	----
	30.0	78.6	----
	----	Average = 79.5	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
55-P	21.0	80.0	81.0
	28.0	79.3	-----
	47.0	78.4	-----
	51.0	78.7	-----
	-----	Average =	79.2
56-P	21.0	80.0	79.2
	31.0	77.5	78.4
	36.0	79.0	78.8
	-----	Average =	78.8
57-P	4.5	77.6	-----
	16.0	72.7	73.0
	24.0	69.4	70.6
	36.5	69.1	68.9
	48.0	70.2	69.0
	-----	Average =	70.4
58-P	11.0	76.2	-----
	25.0	76.5	-----
	33.0	76.8	-----
	48.0	75.2	-----
	-----	Average =	76.2
59-P	8.0	72.5	-----
	12.0	69.2	-----
	32.5	71.9	-----

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
59-P	48.0	66.2	----
	----	Average = 69.1	
60-P	5.0	92.8	92.5
	15.5	90.3	88.0
	23.0	90.2	89.7
	43.0	87.9	88.5
	48.0	87.4	86.5
	----	Average = 88.6	
61-P	10.0	90.9	----
	25.5	87.5	88.2
	31.0	87.3	----
	45.0	86.0	----
	48.0	87.7	----
	----	Average = 87.5	
62-P	3.5	93.3	----
	10.0	91.5	----
	22.0	89.1	----
	35.0	90.1	----
	42.5	88.3	----
	----	Average = 89.2	
63-P	3.5	88.5	----
	8.0	----	----
	18.0	78.2	----

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
63-P	27.0	77.3	----
	37.0	78.2	79.8
	----	Average = 78.2	
64-P	7.0	95.0(AW)	----
	7.0	94.5	----
	16.0	91.9(AW)	----
	16.0	89.7	----
	22.0	89.5(AW)	----
	22.0	89.5	----
	26.0	89.6(AW)	----
	26.0	89.2	----
	38.0	88.5	----
----	Average = 89.2		
65-P	9.0	87.6	----
	12.0	87.6	----
	17.5	88.7	----
	30.0	86.3	----
----	Average = 87.5		
66-P	10.0	90.5	----
	16.0	87.8	----
	21.0	88.1	----
	36.0	86.0	----
----	Average = 87.3		

TABLE VI-A (continued)

<u>Run Number</u> ¹	<u>Hours on Stream</u>	<u>Percent Conversion</u> ²	
		<u>A-1</u> ³	<u>A-2</u> ³
67-P	5.5	86.3	----
	23.0	80.3	----
	28.5	78.7	80.2
	46.5	79.3	----
	----	Average = 79.7	
68-ED	15.0	86.8	86.5
	18.0	87.8	85.9
	24.0	86.2	85.9
	29.0	86.2	85.2
	----	Average = 86.3	
69-ED	16.5	84.6	85.0
	17.0	85.9	84.6
	25.0	84.6	84.0
	28.5	84.3	85.6
	----	Average = 84.8	
70	9.0	98.5	99.0
	11.5	97.0	99.0
	16.0	98.4(WW)	----
	16.0	98.7	98.0
	20.5	96.9(WW)	----
	20.5	96.7	97.5
	36.0	98.4(WW)	----
	36.0	98.0	97.0
	----	Average = 97.8	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
71-ED-1	12.0	92.8	92.5
	17.5	91.2	92.5
	24.5	92.8	90.8
	28.0	91.5	91.2
	-----	Average = 91.9	
71-2	40.0	66.8	-----
	40.0	98.5(S)	-----
	44.0	68.7	-----
	46.0	66.1	-----
	46.0	98.5(S)	-----
	-----	Average = 98.5(S)	
-----	Average = 67.2		
72-ED	16.0	88.7(WW)	-----
	16.0	89.3	88.1
	26.0	88.4(WW)	-----
	26.0	88.1	87.5
	30.0	87.4(WW)	-----
	30.0	87.7	87.1
	32.0	87.2(WW)	-----
	32.0	86.9	88.1
-----	Average = 87.8		
73-ED	12.0	87.7	89.3
	12.0	90.3	-----
	17.0	88.1	87.5

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
73-ED	37.5	89.8(AW)	----
	37.5	87.7	88.1
	39.0	87.7	86.5
	----	Average = 87.8	
74-ED	20.0	85.9	86.2
	20.0	87.9(AW)	----
	28.0	84.7	84.9
	28.0	87.3(AW)	----
	31.0	84.7	86.5
----	Average = 85.5		
75-ED-1	13.0	92.2(AW)	----
	13.0	91.5	90.0
	17.5	93.5(AW)	----
	17.5	92.5	92.5
	17.5	99.4(S)	----
	26.5	91.0	90.5
	26.5	99.8(S)	----
	28.0	90.5	91.5
----	Average = 99.6(S)		
----	Average = 91.3		
75-2	36.0	60.5(AW)	----
	36.0	52.7	52.0
	36.0	95.2(S)	----
	45.0	55.0	----

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
75-2	45.0	94.7(S)	----
	45.0	61.4(AW)	----
	----	Average =	95.0(S)
	----	Average =	53.2
75-3	55.0	64.5	----
	60.0	67.0	66.3
	----	Average =	65.9
76	5.5	91.8	91.3
	23.0	89.8	90.0
	28.5	89.0	90.3
	46.5	88.1	88.5
	----	Average =	89.3
77-ED	18.0	85.0(AW)	----
	18.0	83.7	83.3
	22.5	86.2(AW)	----
	22.5	83.3	84.4
	27.0	84.0(AW)	----
	27.0	82.8	84.0
	32.0	85.2(AW)	----
	32.0	83.7	84.6
----	Average =	83.7	

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
78-ED-1	12.0	90.0	88.8
	18.0	90.3	90.3
	26.0	89.0	89.3
	28.0	90.0	88.8
	----	Average = 89.6	
78-2	33.5	54.0(WW)	----
	33.5	53.3	----
	40.0	96.8(S)	----
	40.0	51.8	----
	44.0	97.5(S)	----
	44.0	52.8	----
	44.0	53.6(WW)	----
	----	Average = 97.2(S)	
----	Average = 52.5		
79-ED	15.0	87.8	88.4
	21.0	86.8	87.5
	24.5	86.2	86.5
	28.5	86.8	87.2
	----	Average = 87.2	
80-ED	13.0	84.0	84.9
	17.5	83.7	84.3
	25.5	84.3	85.2
	29.0	83.5	84.0
	----	Average = 84.2	

TABLE VI-A (continued)

Run Number ⁺	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
81-ED-1	17.5	93.1(AW)	----
	17.5	90.0	91.8
	22.0	95.1	----
	22.0	92.5	92.8
	26.0	91.5(AW)	----
	26.0	89.3	89.3
	30.0	91.5	90.0
----		Average = 90.9	
81-2	36.0	98.9(S)	----
	36.0	79.0	----
	36.0	83.5(AW)	----
	40.5	80.5(AW)	----
	40.5	77.5	----
	49.5	98.5(S)	----
	49.5	79.4	----
	49.5	83.7(AW)	----
----		Average = 98.7(S)	
----		Average = 78.6	
82-ED-1	12.0	91.5	91.8
	16.0	91.8	91.2
	22.0	89.5	89.5
	26.0	90.2	90.7
	----		Average = 90.8

TABLE VI-A (continued)

Run Number ¹	Hours on Stream	Percent Conversion ²	
		A-1 ³	A-2 ³
82-2	36.0	63.0	----
	38.0	61.8	----
	42.0	63.0	----
	----	Average = 62.6	
83	10.0	98.5	99.2
	16.5	98.2	98.7
	25.0	98.4	97.6
	34.0	98.1	----
----	Average = 98.4		
84-1	9.0	90.3	92.5
	13.0	90.0	91.5
	17.5	91.2	92.5
	24.0	90.8	91.0
----	Average = 91.2		
84-2	30.0	92.5	91.0
	36.5	92.5	92.5
	44.0	91.2	92.2
----	Average = 92.0		

TABLE VI-A (continued)

<u>Run Number</u> ¹	<u>Hours on Stream</u>	<u>Percent Conversion</u> ²	
		<u>A-1</u> ³	<u>A-2</u> ³
85	7.5	98.8	----
	14.0	97.2	----
	19.5	97.9	----
	24.0	97.2(WW)	----
	24.0	97.0	----
	28.0	98.0(WW)	----
	28.0	97.5	----
	40.0	97.2	----
	----	Average =	97.4

TABLE VII-A. CATALYST LIFE TEST FEEDSTOCK AND PRODUCT ANALYSES*

Sample Property	Before Hydrotreating (Feedstock)	After Hydrotreating (Product)
A.P.I. Gravity	23.9	29.4
Specific Gravity	0.9114	0.8798
Viscosity, centistokes		
@ 70°F	37.67	8.62
@ 100°F	16.79	5.01
@ 210°F	3.13	1.62
ASTM Color	D 8.0	L 1.5
R.I. @ 20°C	1.547	1.4914
Wt.% Sulfur	0.60	0.02
Wt.% Nitrogen (Total)	0.180	0.041
Distillation (Converted to 760 mm Hg) D-1160**		
I.B.P.	430	180
5%	584	260
10%	608	322
20%	638	449
30%	656	515
40%	673	589
50%	687	645
60%	702	669
70%	716	695
80%	738	730
90%	769	----
95%	791	----
E.P.	795	770
% Recovery	----	88

* The feedstock is Feedstock No. 2, Table I-A. (These analyses were performed by the Continental Oil Company at Ponca City, Oklahoma.)

** Atmospheric to 40%; 10 mm Hg from there to E.P.

TABLE VIII-A. EFFLUENT GAS ANALYSES*

Constituent	Run No. 37 (Sample taken during 86th day of test.)	Run No. 38 (Sample taken during 2nd day of test.)
Hydrogen	92.6	90.8
Oxygen	0.39	0.52
Nitrogen	0.53	0.49
CO ₂ -Ethylene	0.24	0.34
Methane	2.95	2.3
Ethane	0.86	0.81
Propane	0.86	1.4
Isobutane	0.38	1.0
N-Butane	0.49	0.96
Isopentane	0.32	0.72
N-Pentane	0.18	0.42
Hexanes	0.23	0.25
Heptanes Plus	Trace	Trace

*Fractional Analysis by Chromatograph. (Analyses performed by Yapunich, Sanderson and Brown Laboratories at Billings, Montana.)

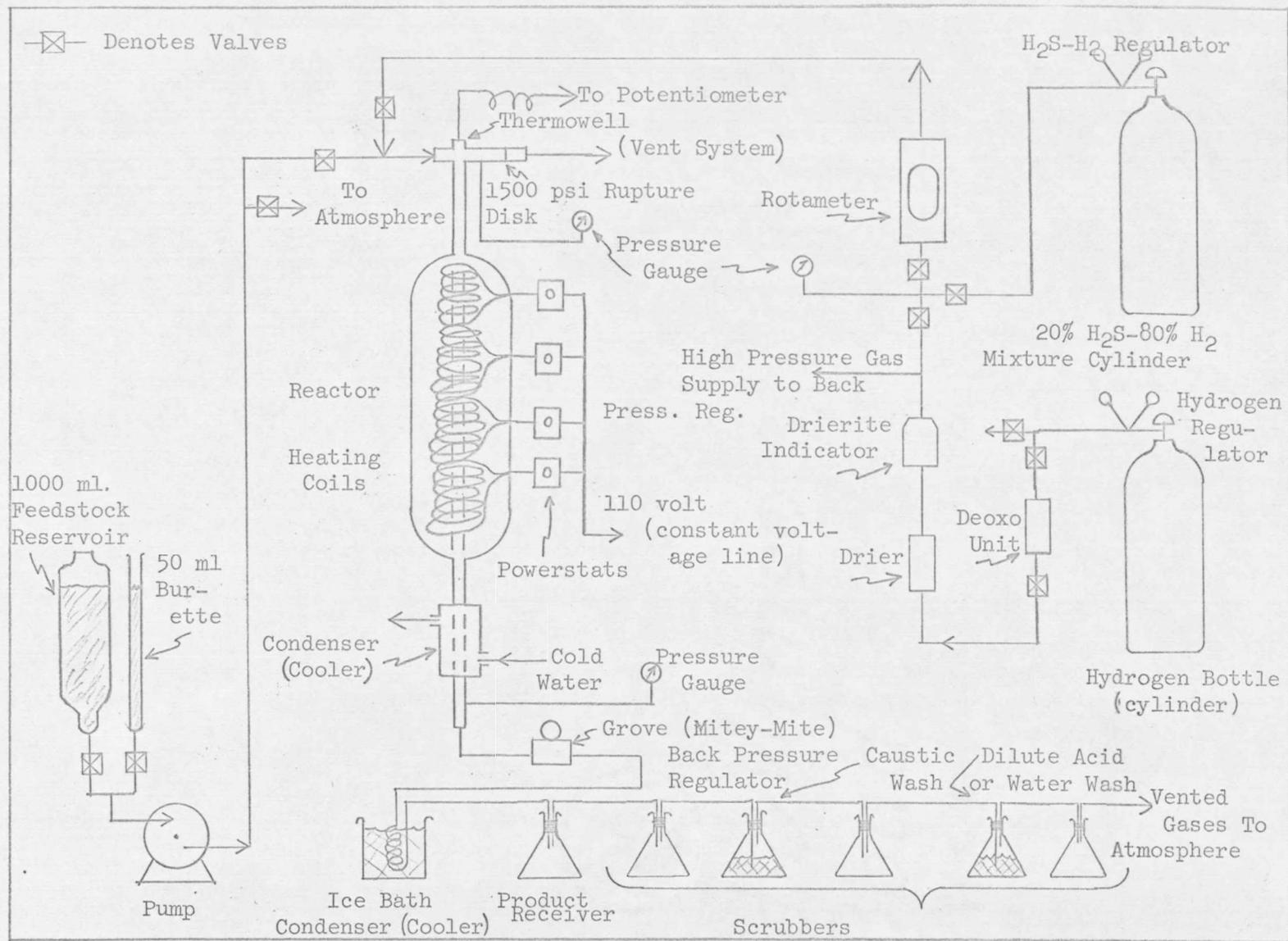


Figure 1-A. Schematic Flow Diagram of the Hydrotreating Unit.

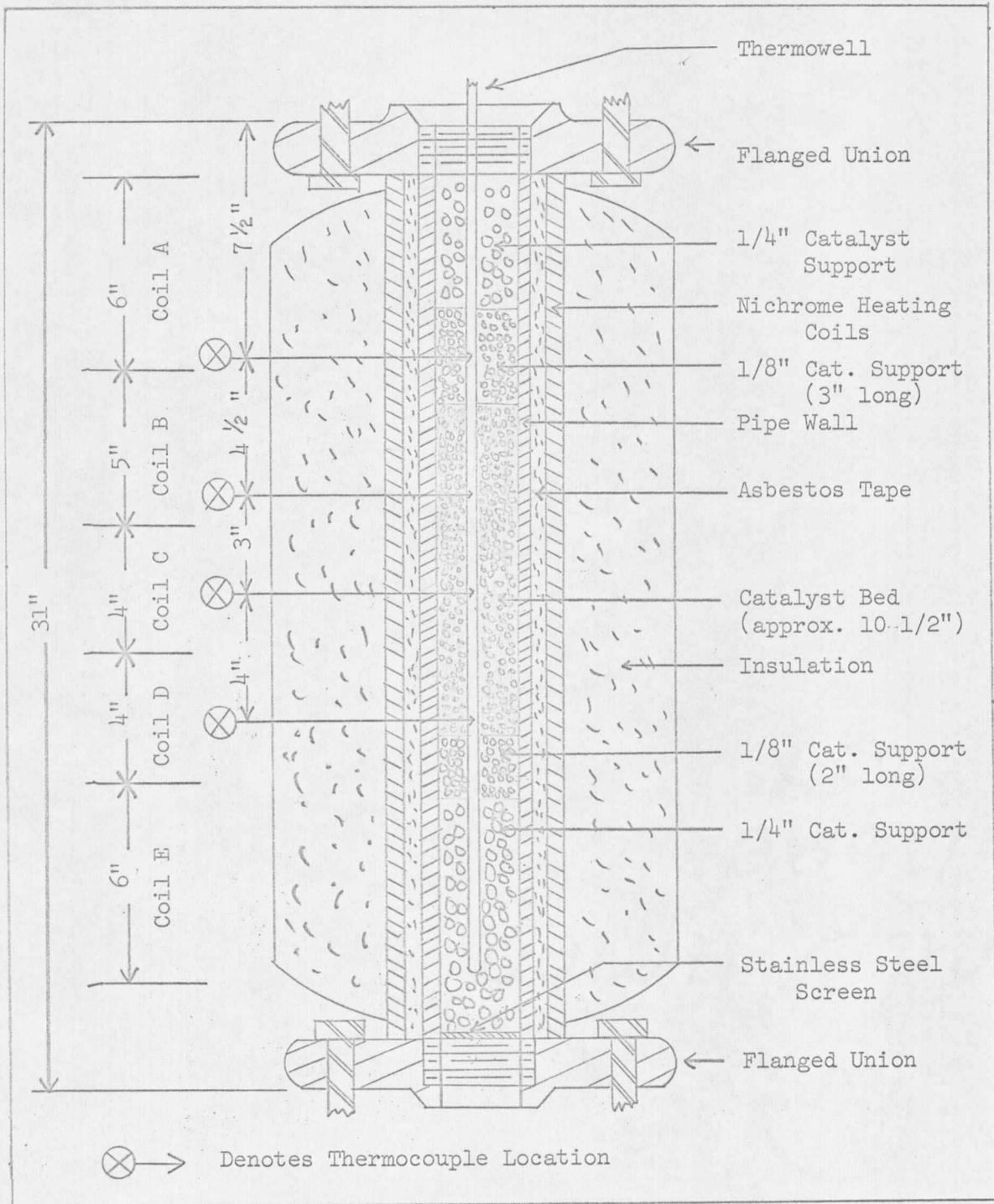
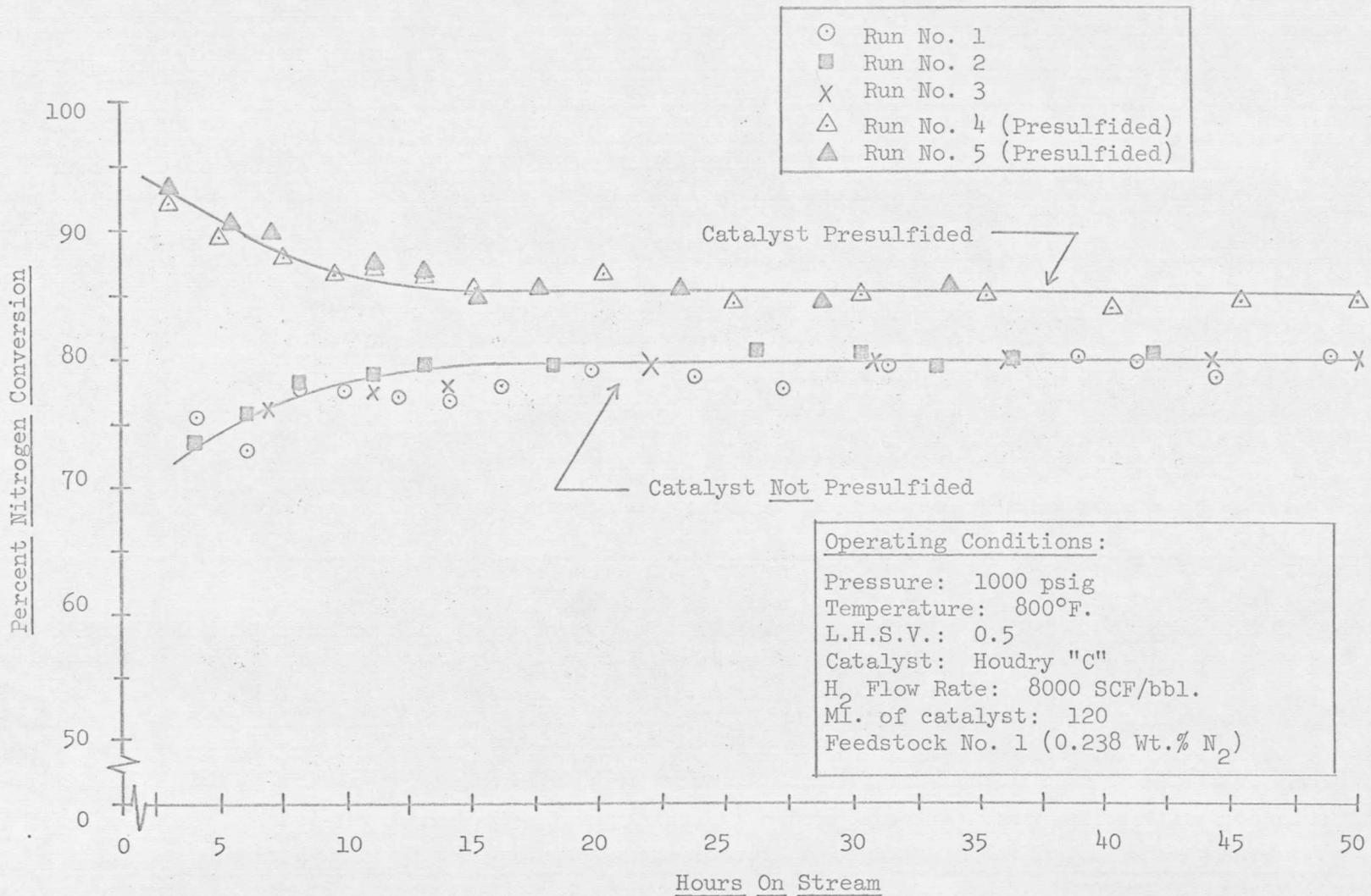


Figure 2-A. Detailed Diagram of the Reactor.



-147-

Figure 3-A. Effect of Hours on Stream and Catalyst Presulfiding on Catalyst Hydrodenitrogenation Activity for a Commercial Cobalt Molybdate Hydrotreating Catalyst.

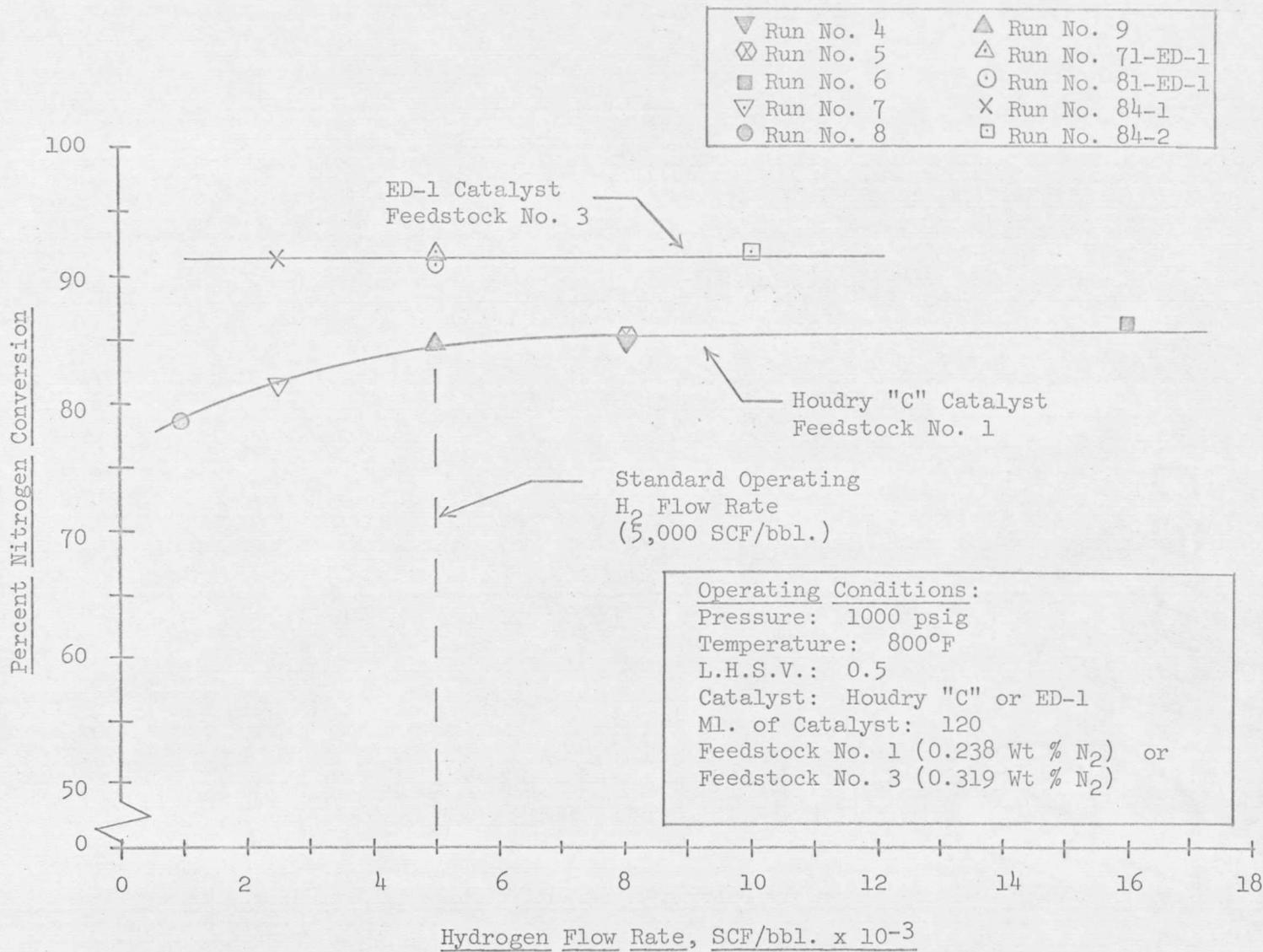
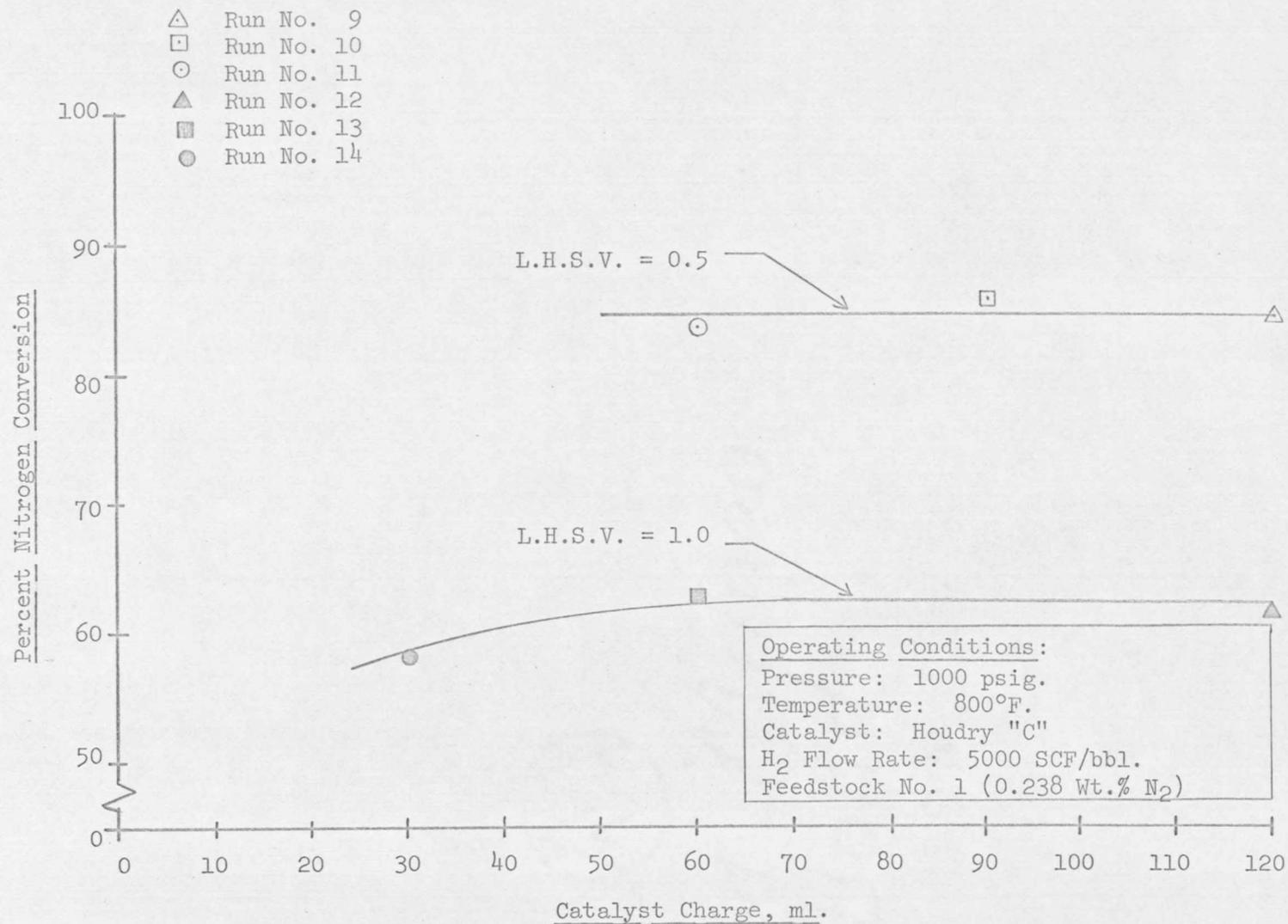
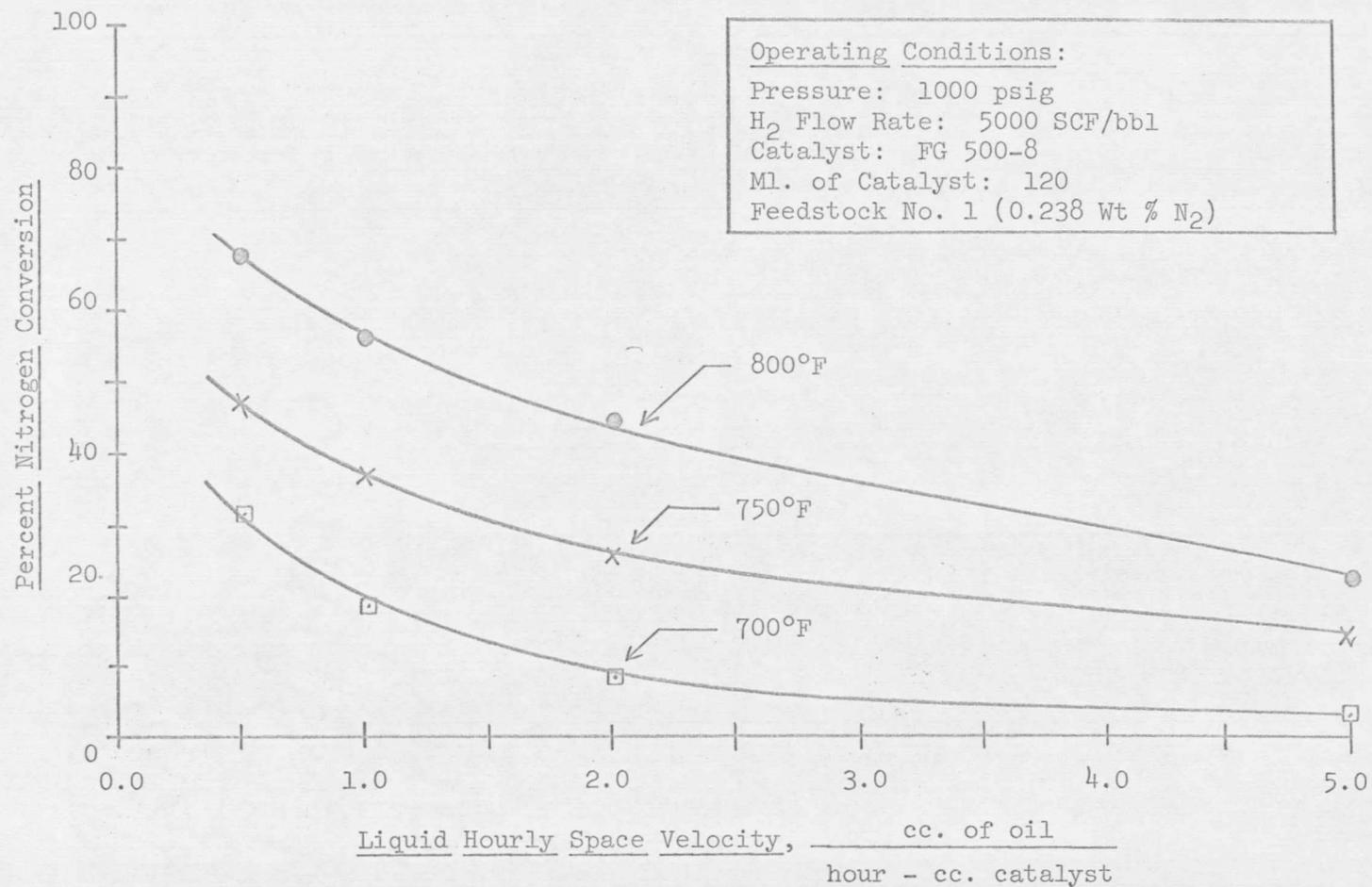


Figure 4-A. Effect of Hydrogen (Hydrotreating) Gas Feed Rate on the Hydrodenitrogenation Activity of the Hydrotreating Catalysts.



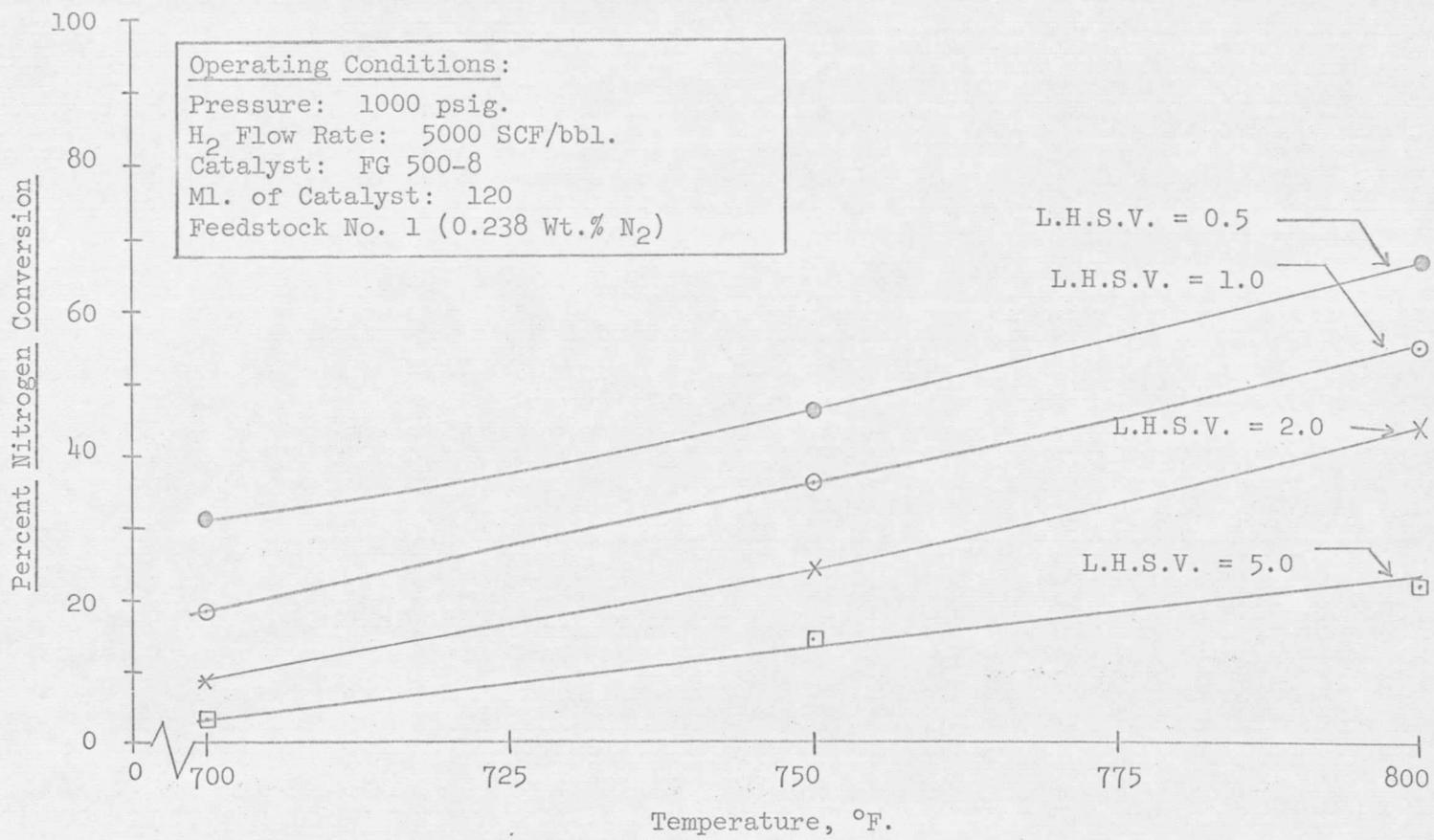
-149-

Figure 5-A. Experimental Test for Film Diffusion Controlling the Catalyst's Activity.



-150-

Figure 6-A. Effect of Liquid Hourly Space Velocity on a Commercial Nickel-Cobalt-Molybdate Hydrotreating Catalyst's Hydrodenitrogenation Activity.



-151-

Figure 7-A. Effect of Temperature on a Commercial Nickel-Cobalt-Molybdate Hydro-treating Catalyst's Hydrodenitrogenation Activity.

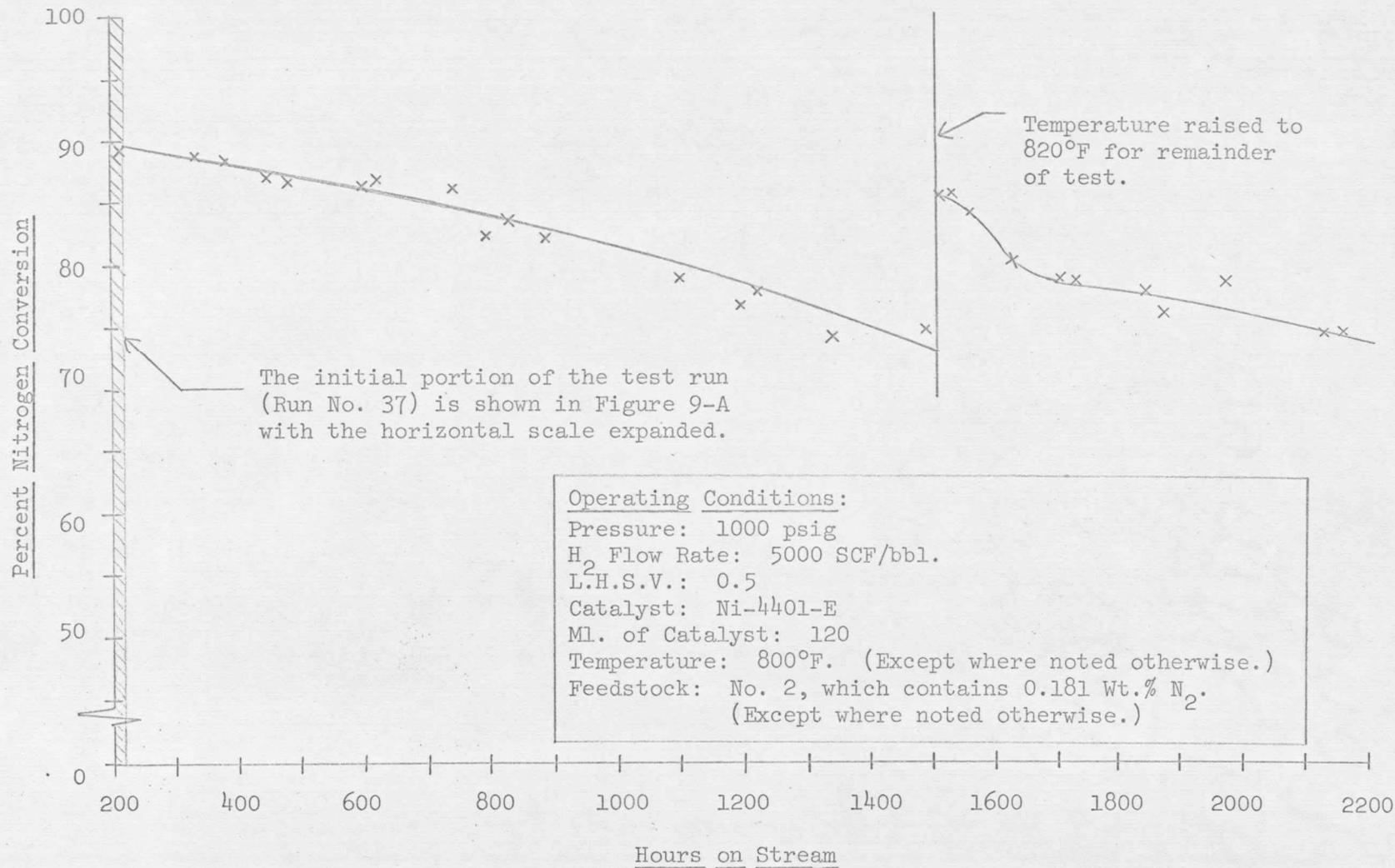


Figure 8-A. Extended (90 Day) Catalyst-Life Test Results for Nickel-Tungsten Catalyst.

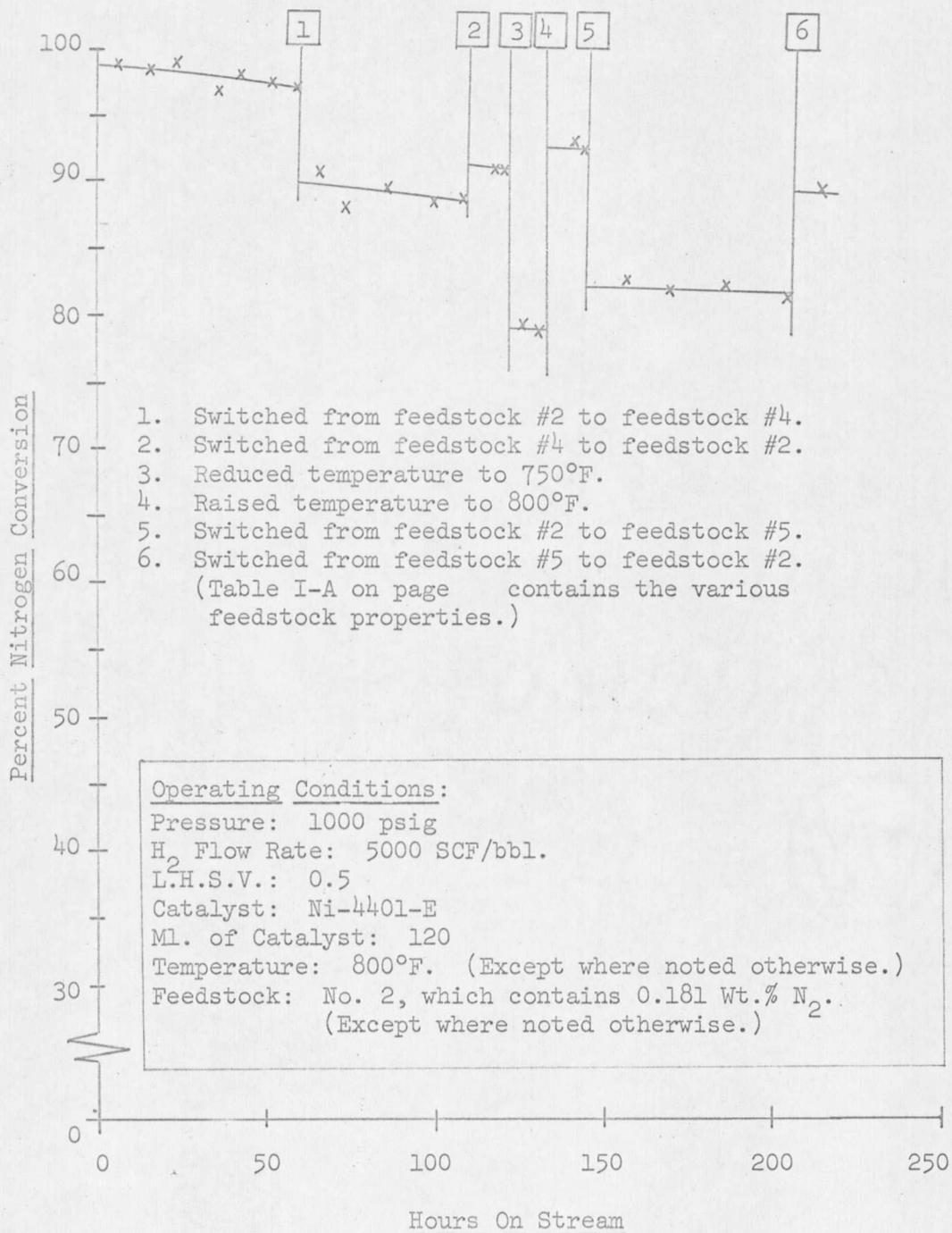
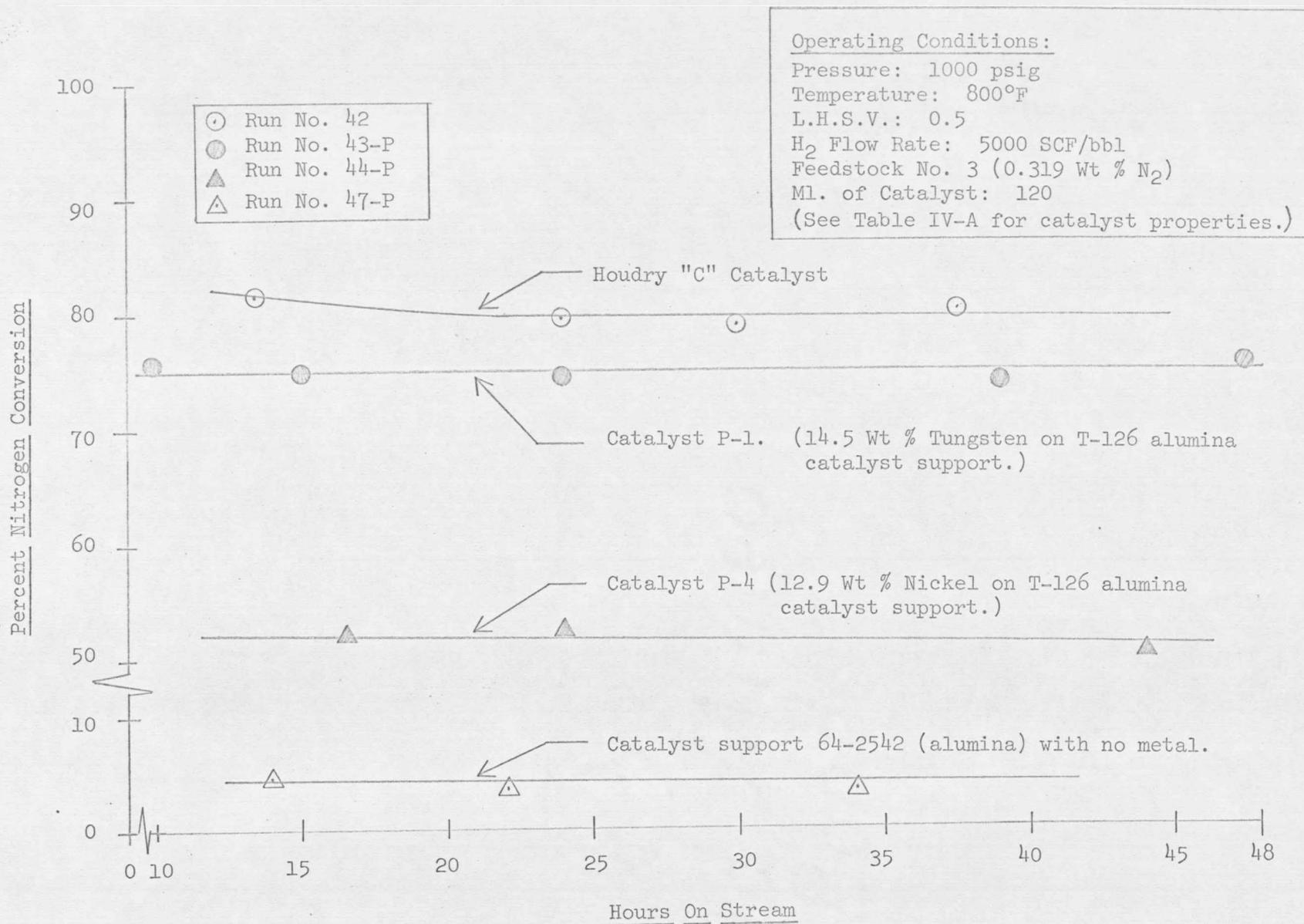


Figure 9-A. Effect of Feedstock Properties and Temperature on Nickel-Tungsten Catalyst Activity for Hydrodenitrogenation. (Extended Catalyst-Life Test -- initial portion.)



-154-

Figure 10-A. "Initial" Preliminary Catalyst Preparation Test Results.

- △ Run No. 45-P (5.5 Wt % Nickel & 13.8 Wt % Tungsten on T-126 support.) -Nickel Impregnated First.
 ▲ Run No. 46-P (4.7 Wt % Nickel & 14.1 Wt % Tungsten on T-126 support.) -Tungsten Impregnated First.

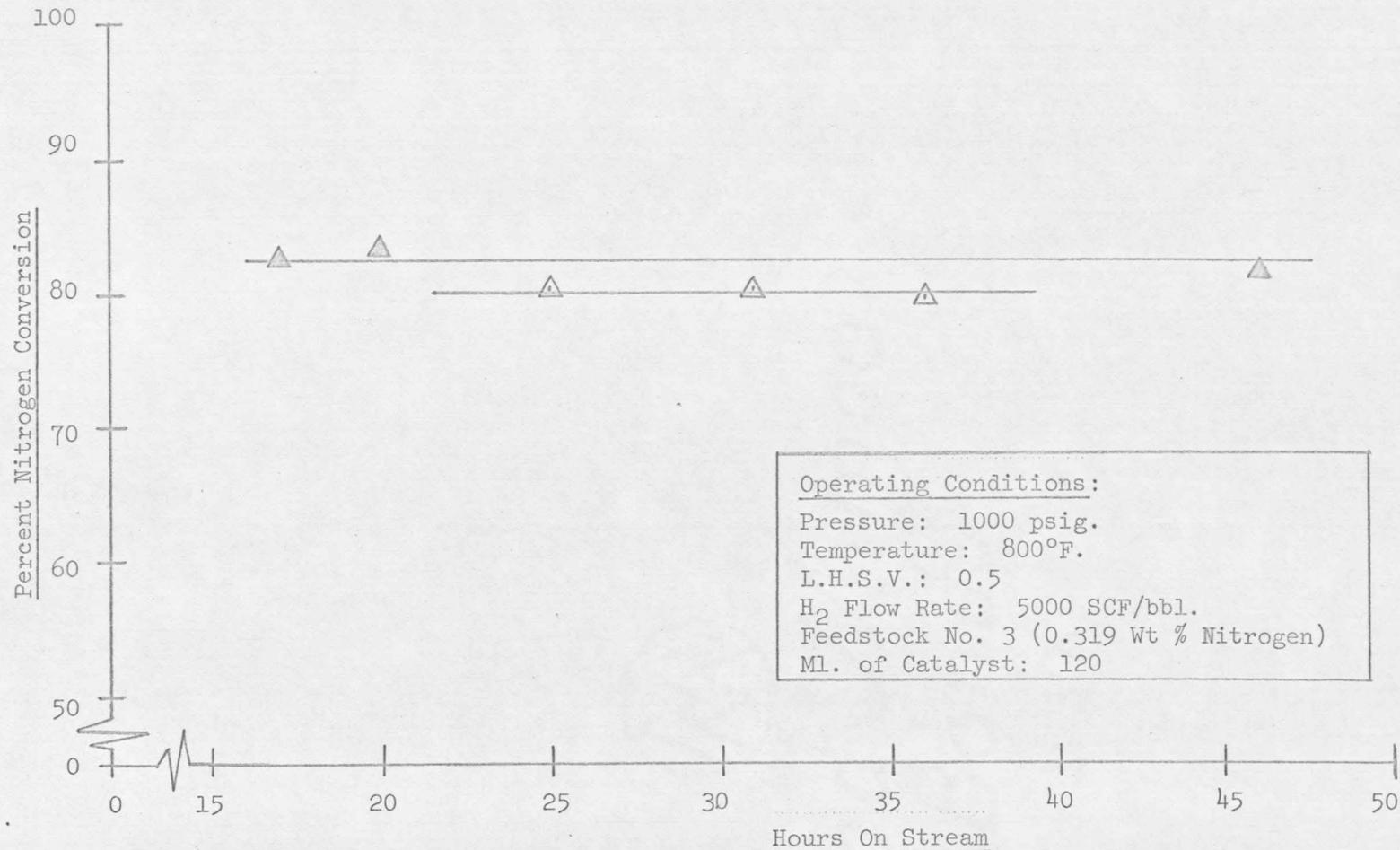
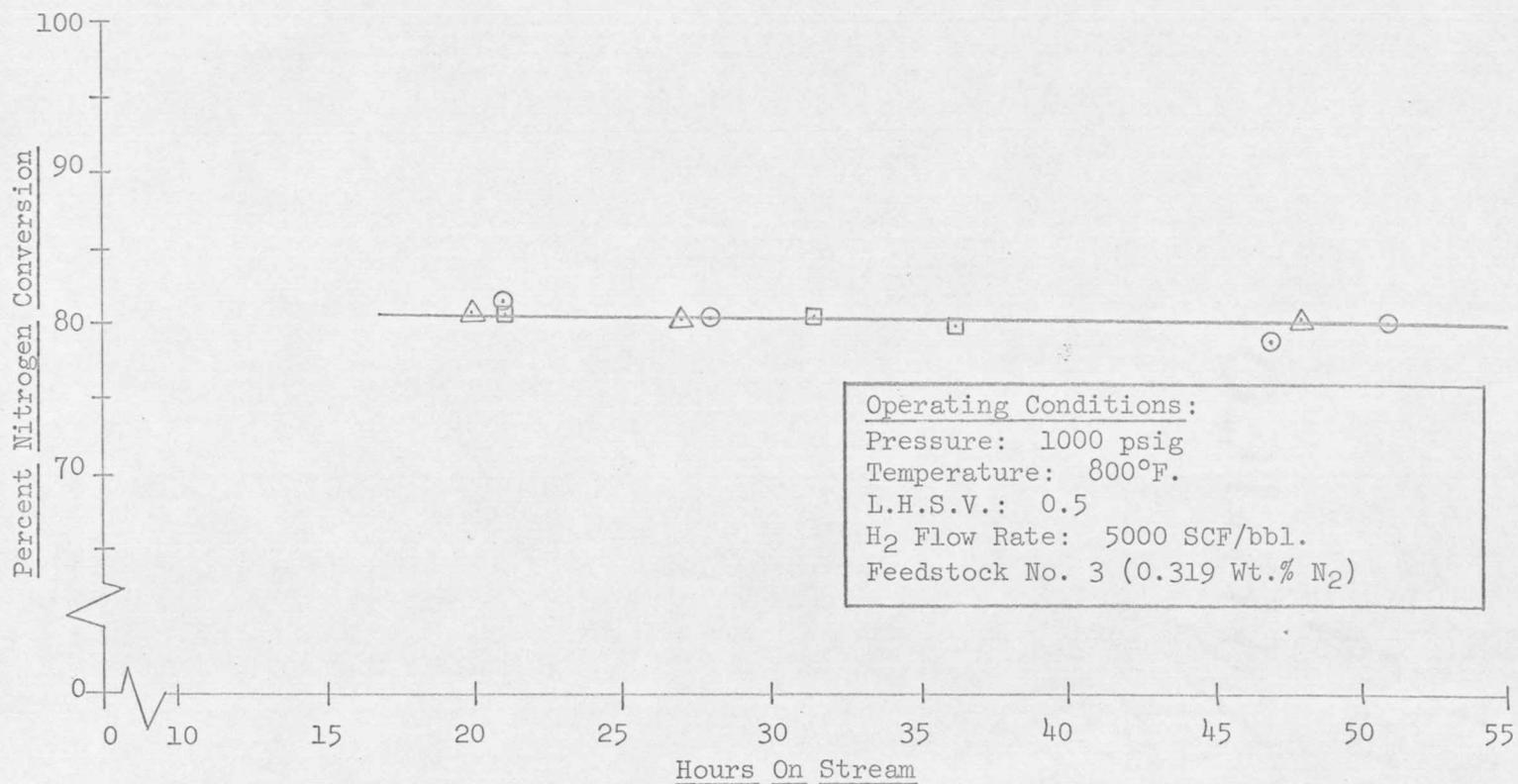


Figure 11-A. Effect of Metal Impregnation Order on the Catalyst's Activity.
(Nickel-Tungsten Catalyst.)

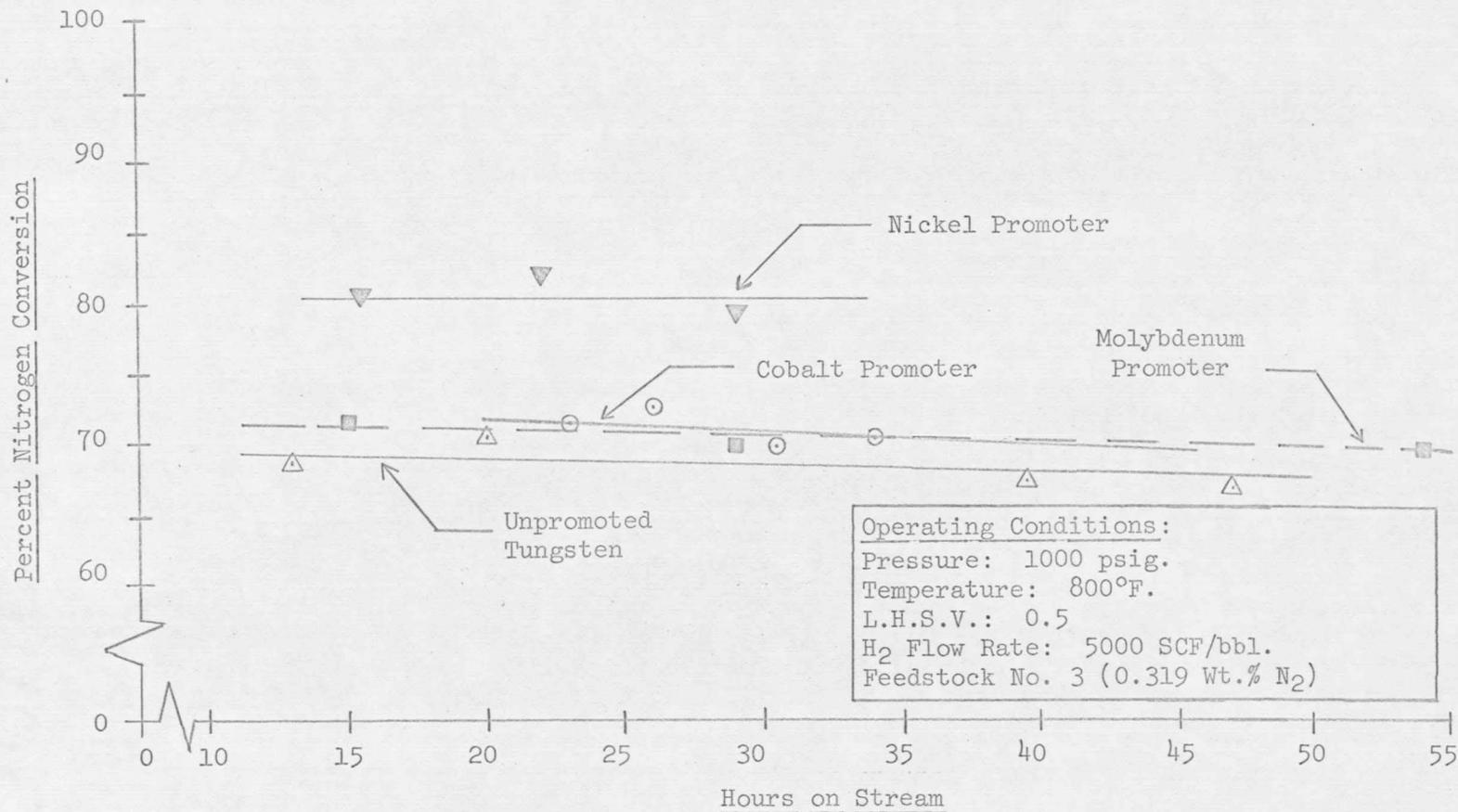
- Run No. 52-P (6.0 Wt.% Nickel & 14.8 Wt.% Tungsten on 64-2542 support.)
- ⊙ Run No. 53-P-1 (6.0 Wt.% Nickel & 15.5 Wt.% Tungsten on 64-2542 support.)
- △ Run No. 53-P-2 (6.0 Wt.% Nickel & 15.5 Wt.% Tungsten on 64-2542 support.)



-156-

Figure 12-A. Effect of Catalyst Preparation Repeatability and Test Run Duplication on the Resulting Catalyst's Activity. (Nickel-Tungsten Catalyst.)

- △ Run No. 48-P (20.2 Wt.% Tungsten on 64-2542 support.)
- Run No. 49-P (8.7 Wt.% Cobalt & 17.8 Wt.% Tungsten on 64-2542 support.)
- Run No. 50-P (9.1 Wt.% Molybdenum & 17.0 Wt.% Tungsten on 64-2542 support.)
- ▽ Run No. 51-P (8.4 Wt.% Nickel & 18.0 Wt.% Tungsten on 64-2542 support.)



-157-

Figure 13-A. Evaluation of Promoters for a Tungsten Type Hydrodenitrogenation Catalyst.

Deviation From Standard Pretreatment

- Run No. 54-P "Standard". (See page .)
- △ Run No. 55-P Catalyst presulfided at 350°F.
- Run No. 56-P Catalyst presulfided by passing sulfur equal to 5 times the weight of the catalyst over the catalyst.
- ▲ Run No. 57-P No catalyst pretreatment. (Metals in oxide form.)
- Run No. 58-P Catalyst presulfided with a solution of CS₂ in cyclohexane at 650°F.
- Run No. 59-P Catalyst pretreated with a solution of pyridine in cyclohexane at 650°F.

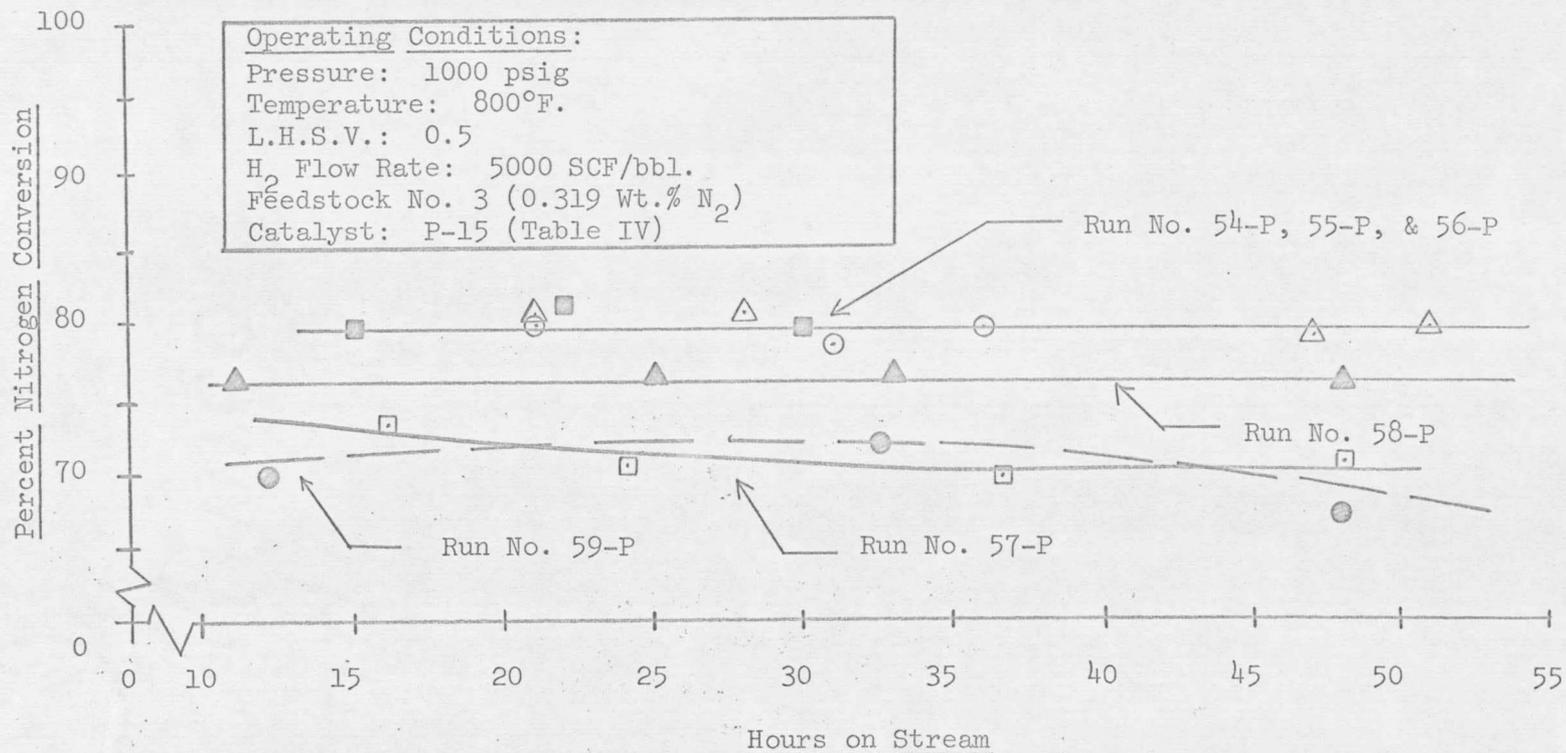


Figure 14-A. Effect of Catalyst Pretreatment Method on Catalyst Hydrodenitrogenation Activity. (Nickel-Tungsten Catalyst.)

- Run No. 46-P (4.7 Wt.% Nickel & 14.1 Wt.% Tungsten on T-126 alumina catalyst support.)
- ▲ Run No. 53-P-2 (6.0 Wt.% Nickel & 14.8 Wt.% Tungsten on 64-2542 alumina catalyst support.)
- Run No. 60-P (5.9 Wt.% Nickel & 15.5 Wt.% Tungsten on Al-1802-E silica-alumina catalyst support.)
- Run No. 62-P (4.7 Wt.% Nickel & 16.4 Wt.% Tungsten on Al-1602-T silica-alumina catalyst support.)
- △ Run No. 63-P (5.3 Wt.% Nickel & 15.7 Wt.% Tungsten on Al-1706-E alumina catalyst support.)

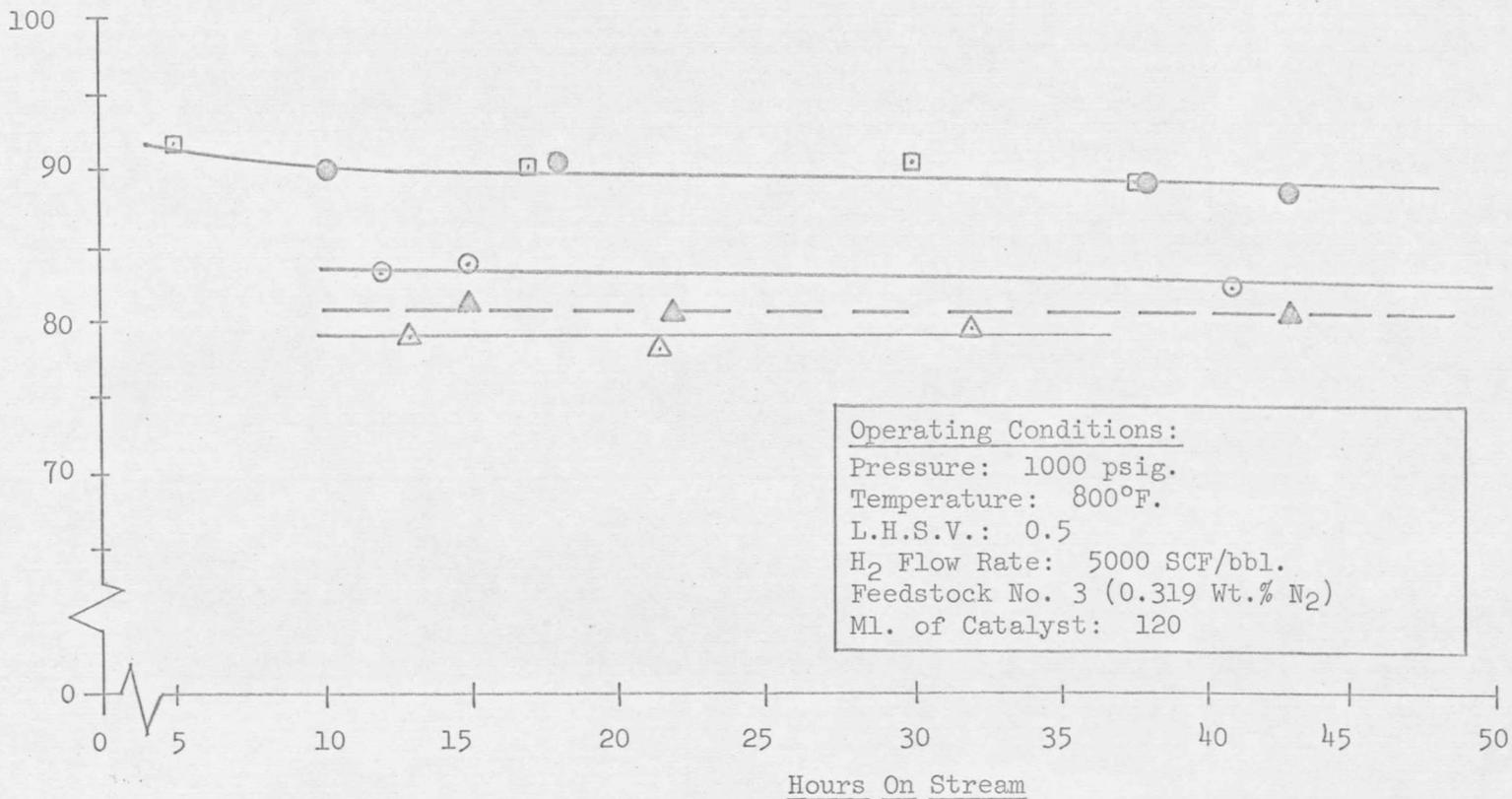
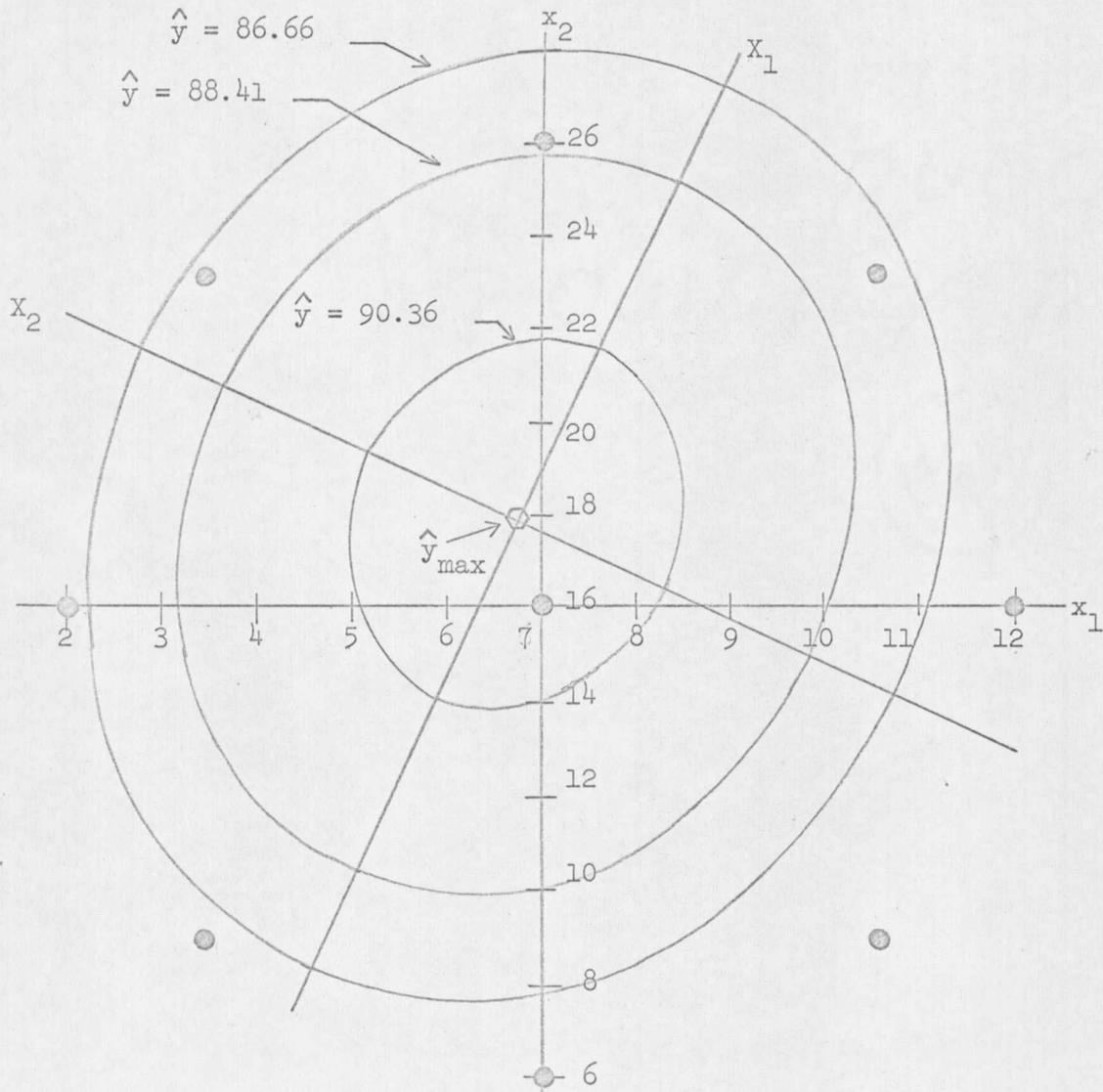


Figure 15-A. Catalyst Support Evaluation (Comparison) for Nickel-Tungsten Hydrodenitrogenation Catalyst.



\hat{y} = the estimated nitrogen conversion, percent.

<u>Operating Conditions:</u>	
Pressure: 1000 psig	
Temperature: 800°F.	
L.H.S.V.: 0.5	
H_2 Flow Rate: 5000 SCF/bbl.	
MI. of Catalyst: 120	
Feedstock No. 3 (0.319 Wt.% N_2)	
Catalysts: "Central Composite ² Rotatable Design Catalysts."	
x_1 = Weight Percent Nickel	● Design Points
x_2 = Weight Percent Tungsten	⬡ Optimum Catalyst Comp.
\hat{y}_{max} = 91.07	

Figure 16-A. Response Surface for Nickel-Tungsten Catalyst.
(See Table IV-A for catalysts tested.)

Run No.	Catalyst	Catalyst Description
□ 37	*Ni-4401-E	6.0 Wt.% Nickel & 19.0 Wt.% Tungsten on <u>silica-alumina</u> support.
● 40	*Ni-4403-E	6.0 Wt.% Nickel & 19.0 Wt.% Tungsten on <u>alumina</u> support.
△ 76	Houdry "C"	3.0 Wt.% CoO & 15.0 Wt.% MoO ₃ on <u>alumina</u> support.
x 83	**ED-1	7.5 Wt.% Nickel & 15.1 Wt.% Tungsten on <u>silica-alumina</u> support.

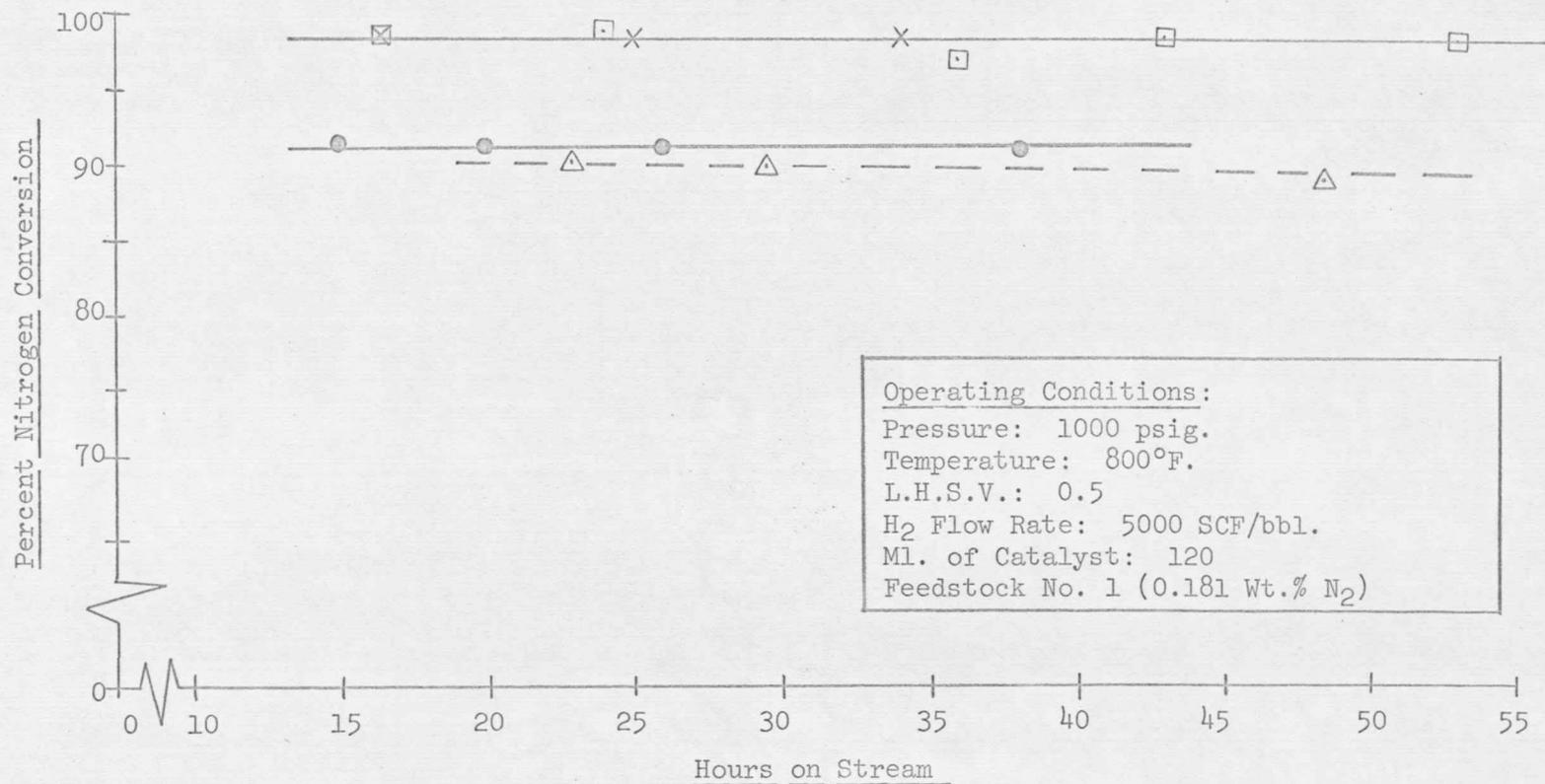


Figure 17-A. Catalyst Hydrodenitrogenation Activity Comparison. (Feedstock No. 1)
 *Harshaw Chemical Co. Catalysts. (Silica-alumina support contains approximately 50 Wt.% SiO₂.)
 **Developed "Optimum Composition" catalyst. (Silica-alumina support contains approximately 6 Wt.% SiO₂.)

Run No.	Catalyst	Catalyst Description
■ 41	*Ni-4401-E	6.0 Wt.% Nickel & 19.0 Wt.% Tungsten on a <u>silica-alumina</u> support.
▲ 42	Houdry "C"	3.0 Wt.% CoO & 15.0 Wt.% MoO ₃ on an <u>alumina</u> support.
⊙ 43-P	P-1	14.5 Wt.% Tungsten on an <u>alumina</u> support.
△ 53-P-1	P-10	6.0 Wt.% Nickel & 15.5 Wt.% Tungsten on an <u>alumina</u> support.
□ (82-ED-1)	**ED-1	7.5 Wt.% Nickel & 15.1 Wt.% Tungsten on a <u>silica-alumina</u> support.
X (71-ED-1)		

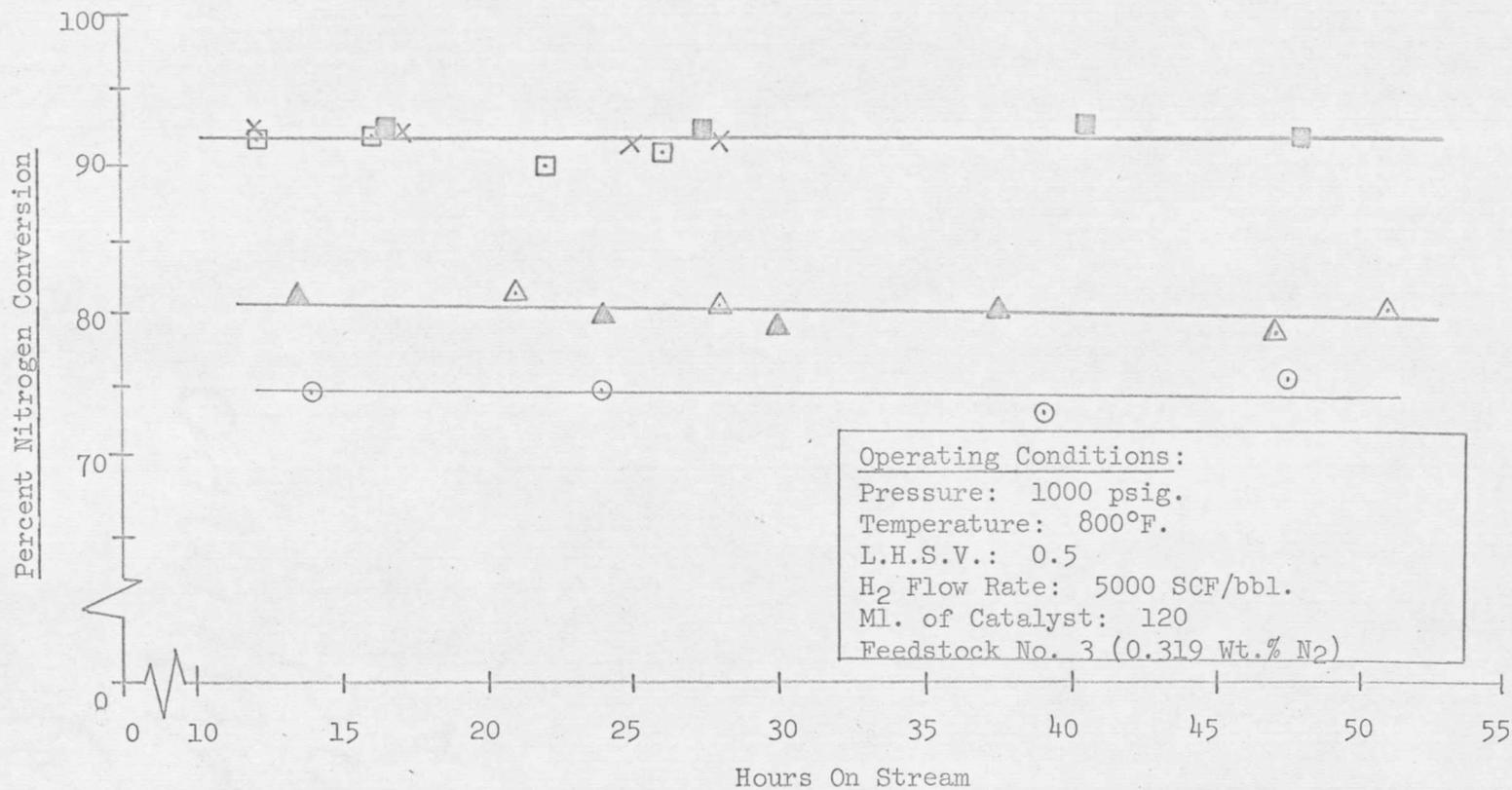


Figure 18-A. Catalyst Hydrodenitrogenation Activity Comparison. (Feedstock No. 3)
 *Harshaw Chemical Co. Catalyst. (Silica-alumina support contains approximately 50 Wt.% SiO₂.)
 **Developed "optimum composition" catalyst. (Silica-alumina support contains approx. 6 Wt.% SiO₂.)

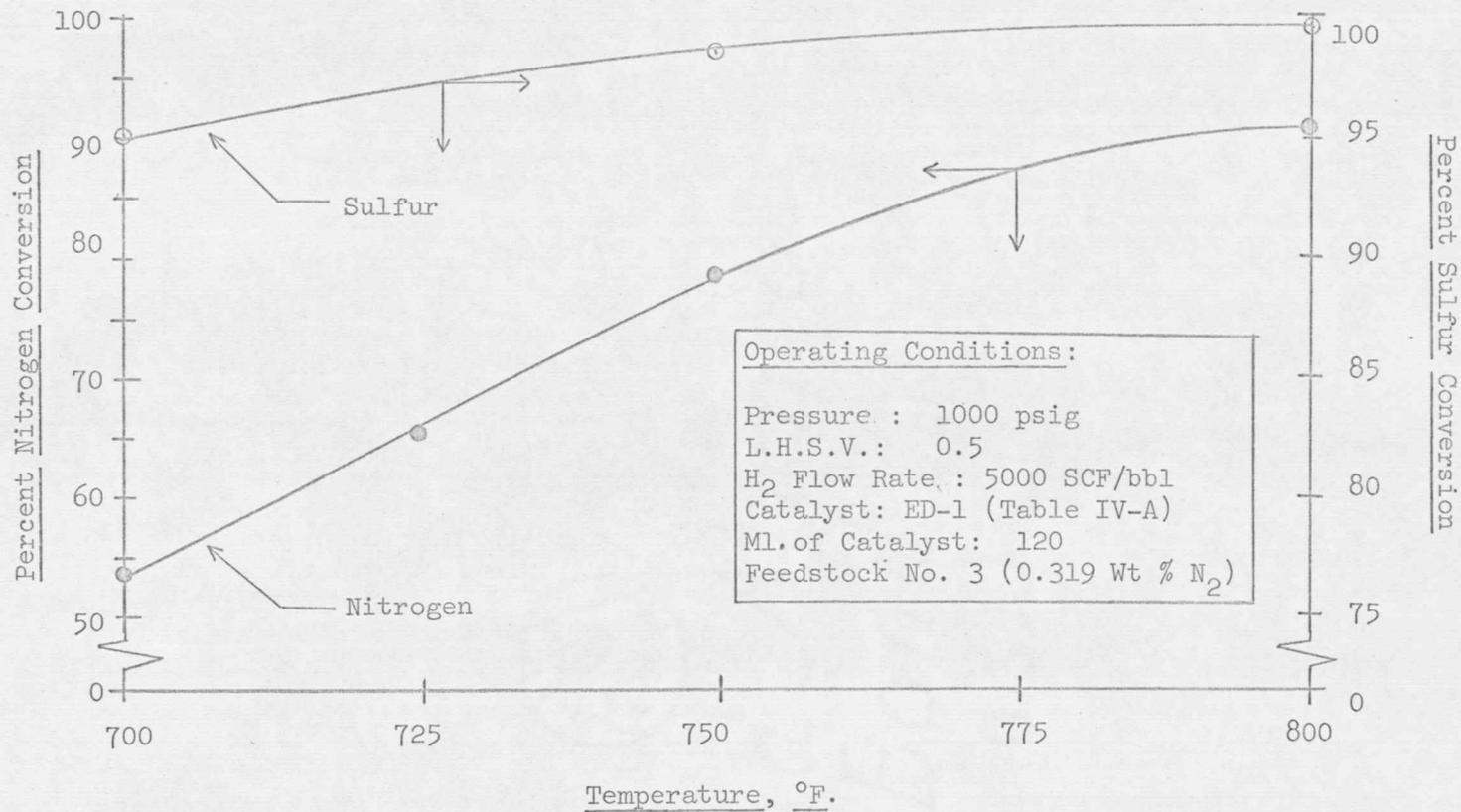


Figure 19-A. Effect of Temperature on the Developed Nickel-Tungsten Catalyst's Hydrodenitrogenation and Hydrodesulfurization Activity.

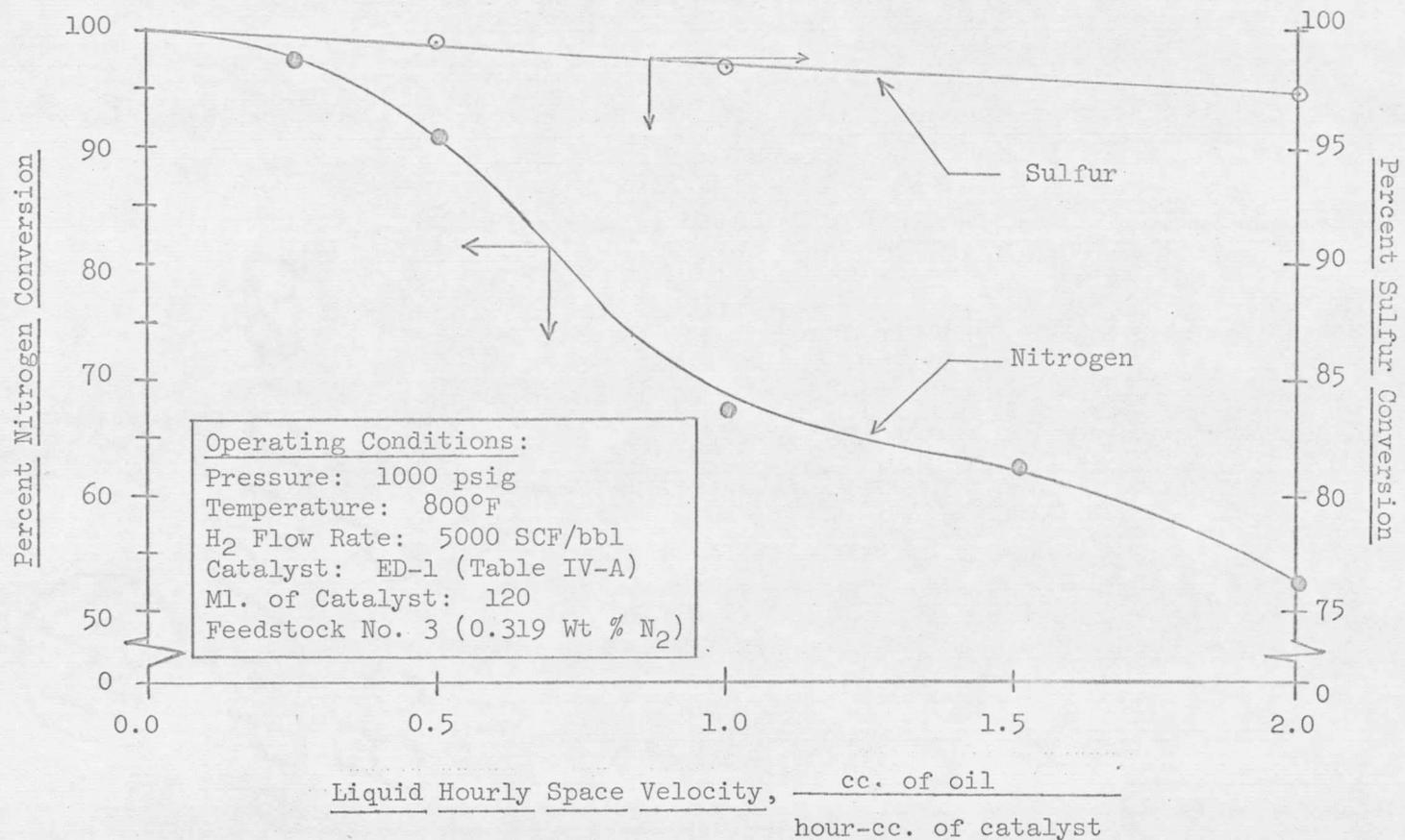


Figure 20-A. Effect of Liquid Hourly Space Velocity on the Developed Nickel-Tungsten Catalyst's Hydrodenitrogenation and Hydrodesulfurization Activity.

LITERATURE CONSULTED

1. Ball, J. S., et al., "Composition of Colorado Shale-Oil Naphtha", Ind. & Engrg. Chem., Vol. 41, pages 581-7, March 1949.
2. Ball, J. S., et al., "Determination of Nitrogen in Shale-Oil and Petroleum", Anal. Chem., Vol. 23, pages 1632-41, November 1951.
3. Ball, J.S., et al., "Nitrogen Content of Crude Petroleums", Ind. & Engrg. Chem., Vol. 43, pages 2577-81, November 1951.
4. Benson, D. B., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1958.
5. Beuther, H., et al., "For Better Hydrodesulfurization Activity of Promoted Molybdenum Oxide-Alumina Catalysts", Ind. & Engrg. Chem., Vol. 51, pages 1349-50, November 1959.
6. Brunk, H. D., "An Introduction to Mathematical Statistics", Ginn & Company, New York, 1960.
7. Burke, D. P., "Catalysts", Chemical Week, Vol. 93, pages 50-64, 17 August, 1963.
8. Casagrande, R. M., et al., "Selective Hydrotreating over Tungsten Nickel Sulfide Catalyst", Ind. & Engrg. Chem., Vol. 47, pages 744-9, April 1955.
9. Cochran, W. G., and Cox, G. M., "Experimental Designs", Second Edition, John Wiley and Sons, Inc., New York, 1957.
10. Cox, K. E., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1961.
11. Deal, V. Z., et al., "Determination of Basic Nitrogen in Oils", Anal. Chem., Vol. 25, pages 426-32, March 1953.
12. Dinneen, G. U., and Bickel, W. D., "Gum Formation in Shale-Oil Naphtha", Ind. & Engrg. Chem., Vol. 43, pages 1604-7, July 1951.
13. Donath, E. E., "Coal-Hydrogenation Vapor-Phase Catalysts", Advances in Catalysis, Vol. VIII, pages 239-292, Academic Press, Inc., New York, 1956.
14. Ellis, C. F., and Lankfork, J. D., "Shale Oil Refining", Ind. & Engrg. Chem., Vol. 43, pages 27-32, January 1951.

LITERATURE CONSULTED (continued)

15. Flinn, R. A., et al., "How Easy is Hydrodenitrogenation?", Hydro-Carbon Processing and Petroleum Refiner, Vol. 42, pages 129-32, September 1963.
16. Hettinger, W. P., et al., "Hydroforming Reactions", Ind. & Engrg. Chem., Vol. 47, pages 719-30, April 1955.
17. Hogg, R. V., and Craig, A. T., "Introduction to Mathematical Statistics", The Macmillan Company, New York, 1959.
18. Hougen, O. A., "Engineering Aspects of Solid Catalysts", Ind. & Engrg. Chem., Vol. 53, pages 509-28, July, 1961.
19. Huffman, H. C., (to Union Oil Company of California), U. S. Patent No. 2,437,532, 9 March, 1948.
20. Jacobson, R. L., and Kozlowski, R. H., (to California Research Corporation), U. S. Patent No. 3,114,701, 17 December, 1963.
21. Keely, W. M., and Maynor, H. W., "Thermal Studies of Nickel, Cobalt, Iron, and Copper Oxides and Nitrates", Jour. of Chem. & Engrg. Data, Vol. 8, No. 3, pages 297-300, July 1963.
22. Kioovsky, J. R., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1962.
23. Kirk, P. L., "Kjeldahl Method for Total Nitrogen", Anal. Chem., Vol. 22, pages 354-8, February 1950.
24. Kirsch, F. W., "Effect of Nitrogen Compounds on Hydrodesulfurization of Petroleum Fractions", Ind. & Engrg. Chem., Vol. 51, pages 1379-80, November 1959.
25. Kline, C. H., and Kollonitsch, V., "Catalytic Activity of Tungsten", Ind. & Engrg. Chem., Vol. 57, pages 53-60, July 1965.
26. Lochte, H. L., and Littmann, E. R., "The Petroleum Acids and Bases", Chemical Publishing Company, Inc., New York, 1955.
27. Maxted, E. B., "Some Recent Advances in Catalysis", Jour. Soc. of Chem. Industry, Vol. 67, pages 93-7, March 1948.
28. McKee, R. H., et al., "Shale Oil", The Chemical Catalog Company, Inc., New York, 1925.
29. Meerbott, W. K., and Hinds, G. P., "Reaction Studies with Mixtures of Pure Compounds", Ind. & Engrg. Chem., Vol. 47, pages 749-52, April 1955.

LITERATURE CONSULTED (continued)

30. Mills, G. A., et al., "Chemical Characterization of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion", Jour. American Chem. Soc., Vol. 72, pages 1554-60, April 1950.
31. Nozaki, K., (to Shell Development Company), U. S. Patent No. 2,744,052, 1 May, 1956.
32. Ostle, B., "Statistics in Research", Iowa State College Press, Ames, Iowa, 1954.
33. Pattison, J. N., et al., "Solid State Reaction Study of Hydrated and α -Aluminas with the Nitrates of Nickel and Cobalt", Jour. of Chem. & Engrg. Data, Vol. 5, No. 4, pages 433-4, October 1960.
34. Processing Notes, "New Hydrocracking Catalyst Promising", The Oil and Gas Journal, Vol. 60, pages 184-5, 26 March, 1962.
35. Richter, F. P., et al., "Distribution of Nitrogen in Petroleum According to Basicity", Ind. & Engrg. Chem., Vol. 44, pages 2601-5, November 1952.
36. Ryffel, J. R., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1960.
37. Sauer, R. W., et al., "Nitrogen Compounds in Domestic Heating Oil Distillates", Ind. & Engrg. Chem., Vol. 44, pages 2606-9, November, 1952.
38. Schreiber, G. P., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1961.
39. Steel, R. G. D., and Torrie, J. H., "Principles and Procedures of Statistics", McGraw-Hill Book Company, Inc., New York, 1960.
40. Stormont, D. H., "How Hydrogen is Faring", The Oil and Gas Journal, Vol. 61, pages 105-13, 11 February 1963.
41. Thompson, R. B., et al., "Stability of Fuel Oils in Storage", Ind. & Engrg. Chem., Vol. 43, pages 935-9, April 1951.
42. United States Bureau of Mines, Report of Investigations 4457, January 1949.

LITERATURE CONSULTED (continued)

43. Voorhies, A., (to Standard Oil Development Company, U. S. Patent No. 2,455,713, 7 December, 1948.
44. Weisser, O., "Sulfide Catalysts, Their Properties and Uses", International Chemical Engineering, Vol. 3, No. 3, pages 388-424, July, 1963.

MONTANA STATE UNIVERSITY LIBRARIES
 3 1762 10005447 5

D378
 F182
 cop.2
 Falk, A. Y.
 Tungsten as a hydrodenitro-
 genation catalyst for petroleum
 oil fractions

	NAME AND ADDRESS
2-19-76	THE [unclear] (unclear) (unclear) (unclear)
	AL [unclear]
	GARY R. HASS (G) BMT Cobleigh 403
R	[unclear]
JUL 2 1976	GARY R. HASS (G) BMT Cobleigh 403
SEP 27 1976	Steve Kujawa Cobleigh 403 Ken Ruan Cobleigh
R	
R	

D378
 F182
 cop.2

