



Cobaltous chloride as a hydrodenitrogenation catalyst
by David Louis Whitcomb

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

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

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

The operating conditions studied were between 670 and 800°F, 800 and 1200 psig, liquid hourly space velocities from 0.25 and 2.0 hr⁻¹, 2000 to 12,000 standard cubic feed hydrogen/bbl oil (SCF H₂/bbl), catalyst compositions from zero to 9.0 percent cobalt, and chlorine-nitrogen ratios from zero to 15.0 atom/atom. Optimum catalyst- composition was 7.0 percent cobalt using Harshaw 1602-T alumina-silica support.

Methylene, ethylene, and propylene chlorides were used as sources of chlorine in the reaction zone. Methylene chloride gave the best -results.

The catalyst activity increased with increasing temperature and pressure, decreased with increasing space velocity, was unaffected by variations in hydrogen treat rates between 2000 and 8000-SCF/bbl, but decreased at hydrogen rates greater than 8000 SCF/bbl. The decrease by using hydrogen rates above 8000 SCF/bbl was probably due to chlorine-hydrogen dilution effects.

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

Hydrogen consumption was determined by analyzing the effluent reactor gases. Consumption varied between 20 and 381 SCF H₂/bbl for the range of operating conditions described above.

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

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

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

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TABLE OF CONTENTS

	Page
List of Tables	vi
List of Figures	vii
Abstract	x
I. Introduction	1
II. Research Objectives	8
III. Experimental	9
A. Introduction	9
B. Reactor System and Operation	10
C. Catalyst Preparation	14
D. Analytical	16
IV. Results and Discussion	21
A. Introduction	21
B. Preliminary Runs	23
C. Catalyst Composition	24
D. Effect of Chlorine-Nitrogen Ratio and Type of Chloride Compound Used in Reactor	26
E. Effect of Hydrogen Flow Rate on Nitrogen Removal	29
F. Effect of Temperature, Pressure, and Space Velocity on Nitrogen Removal	31
G. Chlorine in Product Oil	34
H. Gas Production and Estimated Hydrogen Consumption	36

TABLE OF CONTENTS (continued)

	Page
I. Comparison of Cobaltous Chloride to Other Catalysts	40
J. Desulfurization	42
K. Kinetics of Denitrogenation and Desulfurization	44
V. Catalyst Life Considerations	51
VI. Conclusions	54
VII. Recommendations	57
VIII. Appendix	58
IX. Literature Cited	122

LIST OF TABLES

Table		Page
I	Test Oil Properties	59
II	Properties of Commercial Catalysts and Catalyst Supports Used in Tests	60
III	Experimental Data	61
IV	Fortran II Computer Program for Curve Fitting Used in Life Study Analysis and Gas Chromato- graph Calibration Analysis	73
V	Fortran II Computer Subroutine Used to Plot Gas Chromatograph Calibration Curves	76
VI	Fortran II Computer Program for Determination of Gas Production From Effluent Gas Analysis Using Fitted Calibration Curve	78
VII	Gas Chromatograph Calibration Curve Data for Methane	80
VIII	Gas Chromatograph Calibration Curve Data for Ethane	81
IX	Gas Chromatograph Calibration Curve Data for Propane	82
X	Gas Chromatograph Calibration Curve Data for iso-Butane	83
XI	Gas Chromatograph Calibration Curve Data for n-Butane	84
XII	Typical Output Data From Fortran II Program -- Determination of Gas Production	85
XIII	Data for Least Square's First Degree Fit of Life Study Data From Nine and One-Half Days to End	86

LIST OF FIGURES

Figure		Page
1	Typical Nitrogen Compound Found in Petroleum	6
2	Methane Calibration Curve	80
3	Ethane Calibration Curve	81
4	Propane Calibration Curve	82
5	iso-Butane Calibration Curve	83
6	n-Butane Calibration Curve	84
7	Schematic Flow Diagram of Reactor System	88
8	Detailed Diagram of Reactor	89
9	Preliminary Runs Using Cobaltous Chloride on Alumina-Silica Support	90
10	Solution Concentration Required for Desired Catalyst Impregnation, Harshaw 1602-T	91
11	Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodenitrogenation Catalyst Activity	92
12	Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodesulfurization Activity -- Harshaw 1802-E Support	93
13	Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodesulfurization Activity -- Harshaw 1602-T Support	94
14	Effect of Chlorine-to-Nitrogen Ratio on the Hydrodenitrogenation Catalyst Activity	95
15	Effect of Chlorine-to-Nitrogen Ratio on the Hydrodesulfurization Activity	96
16	Effect of Chlorine-Nitrogen Ratio on Estimated Hydrogen Consumption	97

LIST OF FIGURES (continued)

Figure		Page
17	Effect of Hydrogen Flow Rate on the Hydrodenitrogenation Catalyst Activity	98
18	Effect of Hydrogen Flow Rate on the Desulfurization Activity	99
19	Effect of Hydrogen Flow Rate on Estimated Hydrogen Consumption	100
20	Effect of Chlorine-to-Nitrogen Ratio on Product Gravity	101
21	Effect of Hydrogen Flow Rate on Product Gravity	101
22	Effect of Percent Cobalt on Support, Chlorine-Nitrogen Ratio, and Hydrogen Flow Rate on Weight Percent Chlorine in Product	102
23	Effect of Temperature and Space Velocity on The Hydrodenitrogenation Catalyst Activity	103
24	Effect of Temperature and Space Velocity on the Hydrodesulfurization Activity	104
25	Effect of Space Velocity and Temperature on the Estimated Hydrogen Consumption	105
26	Effect of Pressure and Space Velocity on the Hydrodenitrogenation Catalyst Activity	106
27	Effect of Pressure and Space Velocity on the Hydrodesulfurization Activity	107
28	Effect of Pressure and Space Velocity on the Estimated Hydrogen Consumption	108
29	Effect of Temperature and Space Velocity on Weight Percent Chlorine in Product	109
30	Effect of Pressure and Space Velocity on Weight Percent Chlorine in Product	109

LIST OF FIGURES (continued)

Figure		Page
31	Effect of Space Time on the Hydrodenitrogenation Catalyst Activity, 800°F	110
32	Pseudo Order of Reaction for Hydrodenitrogenation by Differential Analysis	111
33	Test for Pseudo-Second Order Reaction for Hydrodenitrogenation	112
34	Effect of Space Time on the Hydrodesulfurization Activity, 800°F	113
35	Test for Pseudo-Second Order Reaction for Hydrodesulfurization	114
36	Activation Energy	115
37	Typical Gas Chromatograph Analysis Traces of Effluent Gas from Reactor	116
38	ASTM D-158 Distillation for the Feed and Typical Products, 760 mm	117
39	Comparison Between Cobaltous Chloride and Houdry-C Catalysts	118
40	Exploratory Run Using a Nickelous-Cobaltous Chloride Catalyst Compared to Cobaltous Chloride	119
41	Nitrogen Removal as a Function of Time for an Extended Run	120
42	Effect of Changing Operating Conditions on the Hydrodenitrogenation Catalyst Activity	121

ABSTRACT

The catalytic hydrodenitrogenation of a high nitrogen (0.191 wt %) and high sulfur (0.800 wt %) medium California gas oil was studied in a bench scale, packed bed, continuous, tubular reactor. The primary objective of this research was to perform process development studies on the use of a cobaltous chloride alumina-silica catalyst for hydrodenitrogenation. Desulfurization was also studied.

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

I. INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

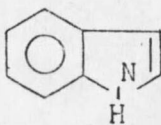
On the basis of spectral evidence and the weakly acidic nature of a specific fraction studied (3), small concentrations of the following classes of compounds could also be present: hydroxyindoles, hydroxycarbazoles, hydroxypyrroloindenes, and dihydropyrroloindenes. This fraction was also the most colored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

petroleum fraction. Aliphatic amides have been extracted from a 430-650°F boiling distillate of Wilmington, California crude oil but represented a small fraction of the material isolated (3).

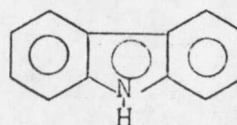
Typical Non-Basic Compounds



Pyrrole



Indole

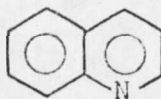


Carbazole

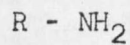
Typical Basic Compounds



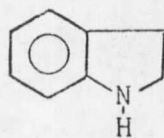
Pyridine



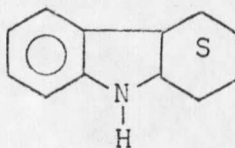
Quinoline



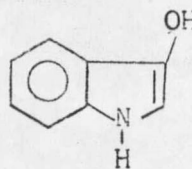
Alkyl Amines



Indoline



Hexahydrocarbazole



2-Hydroxyindole

Figure 1. Typical Nitrogen Compounds Found in Petroleum.

Destructive catalytic hydrogenation seems to be the most selective means of removing the nitrogen from oils since it removes only the nitrogen atoms from the original compounds. There is, then, a definite need to define and develop better and more efficient catalysts for removing nitrogen from petroleum stocks. Since it is well established that the nitrogen compounds present in petroleum are harmful to many refining operations, it would seem that it is best to remove the undesirables from the oil source as early in the refinery processing of the oils as possible.

Investigations (5) conducted at Montana State University have shown the merit of metal chlorides as catalysts. Previous work done with nickel chloride showed a substantial increase in catalyst activity when compared at identical operating conditions to a presently used cobalt molybdate catalyst. Additional study showed that the catalyst activity of cobaltous chloride catalyst was slightly higher than that of nickel chloride.

It was for the above reasons that this study was undertaken to investigate the process development characteristics of a cobaltous chloride-alumina-silica destructive hydrogenation catalyst system using a high nitrogen content medium gas oil.

II. RESEARCH OBJECTIVES

The overall objective of this research work was concerned with the process development of the catalytic hydrodenitrogenation of high nitrogen content gas oils in the presence of a cobaltous chloride alumina-silica catalyst.

Secondary objectives included an investigation of the process variables involved in hydrodenitrogenation and development of a kinetic expression describing the reaction rate in terms of the nitrogen concentration in the gas oil. The process variables investigated included the effect of reactor operating pressure, temperature, liquid hourly space velocity based on oil to catalyst volumes, hydrogen flow rate, catalyst composition, and feed chlorine-nitrogen ratio. Previous work (5) conducted at Montana State University has shown that the last of these variables is important to successful chloride catalyst use. Hence, the method of addition of chlorine to the reaction zone was also investigated.

These objectives were fully or partially realized, depending upon the researcher's estimations of importance, and are discussed later in this paper.

III. EXPERIMENTAL

A. Introduction

Several exploratory runs were made using cobaltous chloride as a catalyst. The purpose of these runs was to determine the effectiveness of the catalyst in nitrogen removal. As a result of these exploratory runs, the reactor system (14) used for earlier studies was found to be totally unacceptable for further use with this catalyst. The system was unacceptable because the accumulation of ammonium chloride, a major reaction product (5), plugged the reactor after only 12 hours of continued use. Falk (14) has shown that in order to obtain useful results, a catalyst line-out of over 12 hours was required. However, interpretation of the exploratory data did show that it would be of value to design and build a new reactor system that would allow for the accumulation of the reaction product.

A schematic diagram, Figure 7, shows the overall flow of the new system. This system included a precooler and heater arrangement that maintained the temperature within the small fittings at the reactor outlet, above the sublimation temperature of ammonium chloride, 335°C (17). The ammonium chloride was then deposited on the walls of the larger diameter section of the precooler, allowing much longer runs to be made.

Additional preliminary runs were then performed. Figure 9 shows the results of two of these runs. The operating conditions and techniques for these runs were based on considerations presented by earlier experimentors (5,14). Interpretation of these results definitely pointed out the probable usefulness of the catalyst and also that the catalyst composition would be an important factor to consider in future work. Consequently, a thorough investigation was undertaken. The following sections expand on the equipment, operational procedures, and analytical techniques used for this investigation.

B. Reactor System and Operation

A detailed diagram of the reactor is shown in Figure 8. It was constructed of a 33-inch length of 1-in. schedule 80, 316 stainless steel tubing. Each end of the reactor tube was threaded and fitted with an appropriate inlet and outlet section. All tubing leading to pressure gauges, pumps, hydrogen supply, fittings, the precooler and thermowell, are 316 stainless steel. The thermowell is mounted axially and extends to within three or four inches of the outlet. It was installed so that it could be located in the center of the reactor. A 6-inch diameter aluminum block used to contain the reactor is heated with seven Nichrome wire heating coils. A pair of two coils (secondary heaters) and a set of three coils (primary heaters) are connected in parallel to give a uniform heat distribution in the block. Each set has an equivalent resistance of 16 ohms and is controlled with a Variac.

The aluminum block is mounted in a 12-in. metal can filled with "Zonolite" insulating material.

The major materials employed consist of barrel-size samples of medium gas oil (see Table I for test oil properties) supplied by Chevron Research Corporation, San Francisco, California, and pure hydrogen supplied by H-R Oxygen and Supply, Inc., Helena, Montana. The major equipment employed consisted of a Hills-McCanna metering type piston pump, a water-cooled condenser, a Grove Mity-Mite back-pressure regulator, a safety head fitted with a 2000 psig rupture disk, a Leeds and Northrup indicating potentiometer, and a Leeds and Northrup recording potentiometer, a high pressure gas rotameter, and a Barber-Coleman on-off temperature controller. The controller is a single point controller, using an iron-constantan thermocouple as the sensing device. It is used to control the temperature at point 2 of Figure 8 with the three primary heating coils. This set of coils heats the major portion of the catalyst zone. Three other equally spaced thermocouple probes inserted in the thermowell are used to measure the temperature profile at other points in the bed.

A normal operating procedure consisted of the following sequence:

- 1) the aluminum block was preheated to the desired temperature; 2) the reactor was loaded with catalyst and placed into the aluminum block;
- 3) the reactor was purged with hydrogen and tested for leaks as it

heated to the desired temperature. (The hydrogen purge was found to be very important and is discussed later in this section.) 4) the feed was started. The feed rate was measured by a 50-ml burette and the hydrogen flow was measured with a high pressure rotameter. The rotameter was calibrated using a wet test meter. In all cases, a catalyst volume of 120 cc was used. The catalyst bed was held in place at the top with 90 cc of 1/4-in. alundum pellets and at the bottom by about 75 cc of 1/4-in. alundum pellets. This centered the catalyst bed in the reactor. A continuous record of the temperature during operation was recorded by the Leeds and Northrup recording potentiometer. The pressure and feed rate were checked periodically and adjusted when necessary.

Typical operating conditions were 800°F, 1000 psig, hydrogen rate of 7,500 SCF/bbl, liquid hourly space velocity (LHSV) of 0.5 hr⁻¹, and a chlorine-nitrogen ratio of 9.0 atom/atom. Most of the experimental data was obtained at these conditions. However, since their effect on catalyst performance was studied, each was varied over a specific range. Temperatures from 670°F to 800°F, pressures from 800 to 1200 psig, hydrogen rates from 2,000 to 12,000 SCF/bbl, LHSV from 0.25 to 2.0, and chlorine-nitrogen ratio from 0 to 15 atom/atom were used.

Two methods were used to obtain samples of the product oil. Neither proved to be superior and consequently both were used. The first method involved obtaining a small volume (15-20 cc) of sample

product for analysis. The second method involved obtaining a large volume (60-120 cc) of sample and subsequently using only a small portion of it for analysis. The time available for taking the sample dictated the method used. Each sample was washed with a dilute solution of NaOH and water and then dried before analyzing. This procedure served to remove any free sulfur from the sample and did not affect the nitrogen analysis.

The effluent reactor gas which was known to contain hydrogen sulfide and some ammonia passed through a diluted NaOH wash and water wash before being emitted through vents to the atmosphere.

The length of each run varied depending on the objective to be accomplished. Figure 9 shows 20 to 25 hours were required to allow this catalyst to line-out. Therefore, each run was at least 25 hours in length and most were 48 to 50 hours long. It was necessary to use the data obtained after line-out to eliminate time as a variable when comparing data. After the initial line-out period, the rate of change of nitrogen removal and hence catalyst deactivation, approaches zero. Figure 42 shows that over a 160-hour period and after repeated changes in operating conditions, the level of nitrogen removal was not changed significantly when compared to the original conditions. In order to obtain meaningful results from those runs during which the operating variables are periodically changed, it was found that after a change

the operating conditions must be held constant for a catalyst age of 4 cc oil/cc catalyst. This corresponds to an elapsed time of eight hours when operating at an oil pumping rate of 1 cc/min and catalyst volume of 120 cc.

The necessity to purge the hot reactor with hydrogen for a sufficient length of time before contacting the catalyst with oil is a very important factor and was not fully realized until this investigation was well underway. This procedure was believed to remove all traces of moisture and oxygen from the system, to activate the catalyst, and played an important part in realizing a high nitrogen removal. This is shown by noting points of identical operating conditions on Figure 11, which relates catalyst composition to nitrogen removal; i.e., at 7.0 percent Co, nitrogen removal is 87 percent, and on Figure 17 which relates hydrogen flow rate to nitrogen removal, at a hydrogen flow rate of 7,500 SCF/bbl, nitrogen removal is 91 percent. A four to five percent increase in nitrogen removal was realized. This is a very substantial increase in nitrogen removal since it represents a decrease from 250 ppm to 175 ppm total nitrogen in the product.

C. Catalyst Preparation

When preparing a catalyst for hydrodenitrogenation studies, it is important to realize that the successful development of a catalyst may depend upon the utilization of as much of the surface area of the

catalyst as possible. For this reason, two catalyst supports and two methods of preparation were studied. The physical and chemical properties of the two alumina-silica catalyst supports can be found in Table II. They have greatly different physical properties and subsequently showed different results. (These results are discussed under the section on Catalyst Composition.)

The method of catalyst preparation involved: 1) support preparation, 2) impregnation, 3) catalyst drying. Since cobaltous chloride is soluble in water, the preparation was relatively simple. The support was first dried at 420°F for 24 hours and weighed to determine the dry weight. A solution of cobaltous chloride, whose concentration had been pre-determined, was poured over the support and allowed to soak into the catalyst pores for 24 hours. A slight vacuum was applied to the impregnation flask to aid the process. Initially, an approximate solution concentration was determined by using pore volume data for the catalyst. After several trials, a curve was drawn giving the solution concentration needed for a desired impregnation level. See Figure 10.

After impregnation, the method of preparation varied. In the first variation, the impregnated pellet was drained and then dried for 24 hours at 420°F . The second variation was developed to determine whether or not the catalyst surface area was being utilized to the fullest extent. It is well known that the catalysts of the type used

in hydrodenitrogenation have a very small external surface area when compared to the internal surface area. It is, therefore, the internal surface area which must be utilized. The second variation involved leaching the external surface area of the catalyst with water before drying. This, in effect, would remove the high concentration of cobaltous chloride that might be blocking the pore mouths at the external surface of the catalyst. The leached catalyst was drained and then dried, as before. Cobalt composition for both variations was determined by assuming the weight gain was anhydrous cobaltous chloride.

Once the catalyst is dried, it is ready to be placed into the reactor.

D. Analytical

Each of the product samples was analyzed for total nitrogen, sulfur, and chlorine. The effluent gas from the reactor was analyzed to determine its composition.

Total nitrogen was determined by the Kjeldahl Method (18,19). Sulfur and chlorine content were determined by the quartz tube combustion method using a Shell design sulfur apparatus (20). Since no previous investigators at Montana State University had used gas chromatography to assist them in describing the operating characteristics of a hydrodenitrogenation catalyst system, an acceptable and reliable procedure was developed.

Philip (21) reported that "Porapak" was successfully used to give a good separation between hydrogen and several light hydrocarbon gases. His column and chromatograph were then used in the preliminary identification of the gases present in the effluent stream. It was found that in addition to unreacted hydrogen, methane, ethane, propane, iso-butane, n-butane, some pentanes, hexanes, and higher molecular weight hydrocarbon gases were present. Also, ammonia and hydrogen sulfide were detected.

After identification of the various gases in the effluent gas stream it was concluded that Philip's chromatograph, equipped with a thermal conductivity (TC) detector, did not offer the operational characteristics and sensitivity desired. Since a flame ionization detector (FID), is much more sensitive in hydrocarbon analysis, an Aerograph 660 chromatograph equipped with a FID was used for all ensuing gas analyses. This chromatograph was better for the gas analyses because as hydrogen was used in the FID, it was not detected and did not interfere with the determination of the other light hydrocarbons even though it was in excess. However, the FID does not detect ammonia or hydrogen sulfide. Therefore, it was assumed that the quantities of these gases were negligible when compared to the quantity of hydrocarbon gases present in the effluent stream. This assumption was quite good considering that ammonium chloride was the major product from nitrogen removal.

To calibrate the column for quantitative analysis, a gas mixture simulating the effluent gas and containing known percentages of methane, ethane, propane, iso-butane, and normal butane was used.

These gases made up about eight percent of the mixture with the remainder being hydrogen. The higher molecular weight hydrocarbon gases were omitted from the analysis because it was found that they were only present in trace amount. Samples of the standard gas were injected into the chromatograph using a 1-ml gas-tight syringe. Injections of 1/4 ml, 1/2 ml and 1 ml were made to simulate various concentrations of the gas. In this way it was possible to calibrate the column in terms of peak height versus volume percent for each compound. Once the percent concentration of each gas was known, the rate of gas production could be determined. A wet test meter was used to determine the effluent gas rate and by knowing the oil rate through the reactor, the pound moles of gas produced per barrel of oil was determined.

Since the calibration curve depended upon temperature and barometric pressure, all analyses were converted to standard calibration curve conditions before final determinations were made.

A digital computer was used to aid in the conversion of the raw peak height data to rate of mole production. A least square polynomial curve fit was used to find a polynomial that fitted the calibration data. This polynomial was then plotted over the range of the data. Once an acceptable polynomial was found, it was a simple matter to re-

late peak height to percent gas and subsequently to mole production. The computer program used for the curve fit is given in Table IV and the program used to plot the calibration data is given in Table V. Tables VII to XI give the calibration curve data and Figures 2 to 6 show the calibration curve for methane, ethane, propane, iso-butane, and n-butane, respectively.

Once the production rate of each gas was known, hydrogen consumption was determined. This parameter could then be related to changes in the various operating conditions. Another computer program was written to calculate the hydrogen consumption and is given in Table VI. A sample output of the data from this program is given in Table XII.

The operating conditions for the Aerograph 660 chromatograph were: 1) carrier gas flow rate of 30 ml/min; 2) temperature of 100°C; 3) hydrogen flow rate to flame of 18 ml/min. The attenuation settings for each of the components were: 1) 3200 for methane and ethane; 2) 1600 for propane; and 3) 800 for the butanes. Nitrogen was used as the carrier gas.

In addition to total nitrogen, sulfur, chloride, and gas analysis, the API gravity of each product sample was measured. ASTM distillations were determined on the feed and several product samples (see Figure 38).

A complete list of the analytical results and operating conditions for each run is given in Table III. Gas production data was not determined for runs in the C or AC series.

IV. RESULTS AND DISCUSSION

A. Introduction

This chapter is devoted to the presentation and discussion of the experimental results of the investigation.

The feed used for all but the preliminary and early exploratory runs was a high nitrogen-content (0.191 wt% N) gas oil designated as CR#8. A summary of the properties of the test oils is given in Table I.

A cobaltous chloride alumina-silica catalyst was investigated for the purpose of hydrodenitrogenation. Several other types of metal chloride catalysts have been studied, with varying degrees of success, for their hydrodenitrogenation activity (5).

Some important observations noted during the investigation are that, in general, a small amount of CoCl_2 impregnated on the catalyst support produced a great improvement in activity. Increasing temperature, pressure, and chlorine-to-nitrogen ratio produced an increasing trend in nitrogen removal. Increasing space velocity decreased nitrogen removal and increasing hydrogen flow rate did not affect nitrogen removal until very high rates were used.

In addition to the product oil, ammonium chloride, hydrogen sulfide, ammonia, methane, ethane, propane, iso-butane, n-butane, traces of pentanes, hexanes, and ethylene were found as reaction products.

Also, a reversal of the ratios of iso- to normal butane from a value greater than one to less than one was observed when the chlorine-to-nitrogen ratio was decreased and when commercial cobalt molybdate catalyst was investigated.

ASTM distillations showed that the boiling range for products obtained when cobaltous chloride was used as the catalyst did not differ significantly from the boiling range when a commercial cobalt molybdate catalyst was used.

The trends in sulfur removal closely followed the trends in nitrogen removal but at a lower percent removal.

A re-statement of the objectives is in order. The objectives included investigating the process variables -- temperature, pressure, space velocity, hydrogen flow rate, catalyst composition, and feed chlorine-nitrogen ratio on the activity of the cobaltous chloride alumina-silica catalyst; and developing kinetic expressions describing the rate of impurity removal in terms of the impurity concentration. Nitrogen removal was the principal interest, but sulfur removal was also investigated.

The extent to which the objectives were realized is discussed in the following sections.

B. Preliminary Runs

The purpose of these runs was to familiarize the investigator with the operation of the equipment and to discover whether the use of cobaltous chloride as a catalyst warranted additional study. As can be seen from Figure 9, the level of nitrogen removal was 93 percent for a 7.2 percent Co (as anhydrous cobaltous chloride) catalyst, and 89 percent for a 6.0 percent Co catalyst. These runs were 50 hours plus in length and showed that over a short period of time a high level of nitrogen removal was realized. Therefore, a thorough study was warranted. In addition, it was realized that the amount of impregnated cobalt was definitely an operating variable.

A definite catalyst line-out period was also found to be necessary. Catalyst line-out is required to allow the catalyst to become saturated with oil and equilibrium established. Line-out is a function of catalyst age based on unit of oil per unit of catalyst.

The time necessary for catalyst line-out in the preliminary runs was 25 to 30 hours. Since they were conducted at a $LHSV = 0.25 \text{ hr}^{-1}$, a catalyst age of 10 to 12 ml oil/cc catalyst was realized for line-out to occur. Since this was the minimum catalyst age used in all future runs, time was not an important variable unless runs were made over an extended period.

A chlorine-nitrogen ratio of 9.0 atom/atom was used. This value was selected after considering ranges used in previous work (5).

C. Catalyst Composition

Tests were made of catalysts containing various amounts of cobaltous chloride to determine the optimum catalyst composition with respect to nitrogen removal. Two catalyst supports were used and compared in this part of the study. The operating conditions used for the entire series of runs were 1000 psig, 800°F, LHSV of 0.5 hr⁻¹, chlorine-nitrogen ratio of 9.0 atom/atom, and 7500 SCF H₂/bbl oil as the hydrogen rate. In all cases the nitrogen removal is based on samples taken after or at a catalyst age of 20-24 cc oil/cc catalyst. This represents approximately 48 hours on stream and is more than sufficient for catalyst line-out. The results of these tests are shown in Figure 11, which presents percentage nitrogen removal as a function of percent cobalt on the catalyst for each of the catalyst supports studied.

As can be seen from Figure 11, a small amount of cobalt increased the activity of the catalyst made from Harshaw 1802-E quite appreciably but did not have the same effect on the activity of the catalyst made from Harshaw 1602-T. Also, it can be seen that the various methods of catalyst preparation did not affect the performance of the catalyst. This indicates that the capability of the entire surface area of the catalyst was used -- at least at the optimum catalyst composition.

The percent nitrogen removal for the catalyst made from Harshaw 1802-E increased from 65 at zero percent cobalt to about 80 percent at

3.5 percent cobalt. It did not increase above 80 percent removal when the percent cobalt was increased to about 9 percent. The optimum nitrogen removal for Harshaw 1802-E was then 80 percent at 3.5 percent cobalt.

For Harshaw 1602-T, nitrogen removal increased from 77 percent at zero percent cobalt to 86 percent at about 7 percent cobalt. This increase in removal was linear up to 7 percent cobalt and did not change from 86 percent as the catalyst composition was increased to 9 percent cobalt. Consequently, the optimum catalyst composition for Harshaw 1602-T was found to be about 7 percent cobalt and yielded an 86 percent nitrogen removal. This represents a final product concentration of about 250 ppm and is well below the final product concentrations achieved by other workers using similar feedstocks (5,14).

The API gravity of the product was not significantly affected by increasing the percent cobalt on the support. The Harshaw supports yielded a product with API gravities of 26.5 and 27.6 for 1802-E and 1602-T, respectively. The gravity then increased slightly to about 27.5°API for 1802-E and 28.0°API for 1602-T, where it remained constant as percent cobalt on the support was increased.

Flinn and co-workers (12) believe that simple hydrocracking reactions are a final step in hydrodenitrogenation mechanisms. This is not surprising since most hydrodenitrogenation catalysts are made by

impregnating a metal promoter on an alumina or alumina-silica base and various alumina-silicas are the major catalytic cracking catalysts. Therefore, if the feed gravity, 23.9°API, is compared to the product gravities for the unpromoted alumina-silica and promoted alumina-silica base, the major part of the cracking of the stock has occurred as part of the reaction between the catalyst base and feed. The promoter, cobaltous chloride, has not contributed significantly to the change in API gravities of the feed and product.

As impurity removal is one of the underlying objectives of this investigation, the support and catalyst composition giving the highest nitrogen removal was selected for use in all subsequent runs. Therefore, a large batch of catalyst containing 7 percent cobalt impregnated on Harshaw 1602-T was prepared and used to investigate the effects of the remaining operating conditions on nitrogen removal.

D. Effect of Chlorine-Nitrogen Ratio and Type of Chloride Compound
Used in Reactor

The necessity to add some form of organic chloride to the feed of a metal chloride catalyst system was first observed by McCandless (5). He also observed that ammonium chloride was the major reaction product involved in combining with and hence removal of nitrogen from the feed gas oil. McCandless found that methylene chloride was adequate as a means of supplying chlorine to the reaction zone of various metal

chloride catalyst systems. The preliminary runs made with cobaltous chloride showed that it was acceptable for that system, also. Therefore, methylene chloride was used in this study to determine the effect of chlorine-nitrogen ratio on nitrogen removal.

Test runs were made using chlorine-nitrogen ratios of 0.0, 3.0, 6.0, 9.0, 12.0, and 15.0 atom/atom to determine the effect of this variable on nitrogen removal. Figure 14 shows the result of this study. Nitrogen removal begins at 67 percent when no methylene chloride is present in the feed and increases to 88 percent when the chlorine-nitrogen ratio is 15.0. At a chlorine-nitrogen ratio of 9.0, the nitrogen removal is 86 percent. Increasing the chlorine-nitrogen ratio above 9.0 does not significantly increase the nitrogen removal. Therefore, a chlorine-nitrogen ratio of 9.0, well above the stoichiometric ratio required for combination with each nitrogen atom, was used as the optimum value.

Nitrogen removal was also studied when ethylene and propylene chloride were used to supply chlorine to the reaction zone. Neither of these compounds were as successful as methylene chloride in producing a satisfactory nitrogen removal. Figure 14 shows that for ethylene and propylene chloride at the optimum chlorine-nitrogen ratio of 9.0, only an 80 percent removal was achieved.

As a result of these observations, it was apparent that the active form of the catalyst was a chloride form. When the feed chlorine-

nitrogen ratio was zero, the catalyst was very unreactive for nitrogen removal due to the depletion of the chloride available for reaction. Addition of methylene chloride to the feed produced a sharp increase in catalyst activity, probably because it reacted with the deactivated catalyst offering a step for regeneration. It would not seem apparent that the compound used in the regeneration would be an important factor. However, this is not the case. Ethylene and propylene chloride regeneration do not produce the same level of nitrogen removal. This could be due to the relative stabilities of the organic compounds in question. The heat of formation, ΔH_f^0 , for methylene and ethylene dichloride are -21 Kcal/mole and -25.1 Kcal/mole, respectively (17). If ΔH_f^0 of propylene chloride is estimated as -29.7 Kcal/mole by assuming the addition of a methyl group to ethylene dichloride, then methylene chloride is the least stable of the three and probably the most reactive. Therefore, in all subsequent runs, methylene chloride was used as a means of supplying the chloride to the reaction zone.

The effect of chlorine-nitrogen ratio on the API gravity of the product is shown in Figure 20. The product gravity increased sharply from 26.5°API to about 27.5°API when a small amount of organic chloride was added to the feed. This indicates that the chloride compound was not overly involved in any hydrocracking reactions other than those involving nitrogen removal.

E. Effect of Hydrogen Flow Rate On Nitrogen Removal

At this point in the study, the method of preparing for each run was changed. The reactor system was purged with hydrogen for 12 hours before contacting the catalyst with oil. This procedure removed any moisture and air from the system and probably activated the catalyst. No speculation can be offered as to what might be involved in the activation if indeed it is an activation, because very little is understood about the active surfaces of hydrodenitrogenation and hydrodesulfurization catalysts (23). As a result of this new procedure, a 4-5 percent increase in nitrogen removal was realized. This is a very substantial increase since it represents a decrease from 250 to 175 ppm total nitrogen in the product. This method was then used in all subsequent runs and explains the abrupt increase of optimum nitrogen removal from 86 to 90.5 percent apparent on several figures.

Several tests were made to determine the effect of hydrogen rate on nitrogen removal. Hydrogen rates from 2000 to 12,000 SCF H₂/bbl were used.

As seen from Figure 17, the percent nitrogen removal is constant at 91 percent as the hydrogen rate is increased from 2000 to about 8000 SCF/bbl. At 8000 SCF/bbl it begins to decrease slightly and at 12,000 SCF/bbl is about 85 percent. Hydrogen flow rates of less than 2000 or greater than 12,000 SCF/bbl were not studied.

The results of these tests are somewhat unusual but not without explanation. Falk (14) has reported that to test for external film diffusion effects the hydrogen flow rate should be varied and nitrogen removal determined. If film diffusion is rate controlling, the nitrogen removal should increase with increasing hydrogen flow. He reports that for a study using a cobalt-molybdate sulfide catalyst, nitrogen removal increased to a maximum at about 4000 SCF H₂/bbl and remained constant at hydrogen rates up to 16,000 SCF/bbl. On the surface there seems to be a contradiction between these data. However, this is not the situation.

Considering the chloride catalyst system, a new parameter can be presented. This parameter will define the concentration of the organic chloride in the reaction zone and is the chlorine-hydrogen ratio. Since the organic chloride has already been shown to be important to the reaction involving nitrogen removal, the concentration of the chloride in the reaction zone will be a function of the amount in the feed and the hydrogen rate. The hydrogen rate is important because at high rates the large volumes would tend to dilute the chloride concentration since the methylene chloride would probably be in the vapor phase at the operating temperature of the reactor. The critical temperature of methylene chloride is 456°F (24). The chloride-to-hydrogen ratio then decreases as hydrogen rate increases for a constant oil feed rate and methylene chloride concentration. Above a hydrogen rate of 8000 SCF/bbl, the

chloride diffusion to the surface of the catalyst probably becomes the rate controlling step in the mechanism of nitrogen removal in the system.

Figure 21, effect of hydrogen flow rate on product gravity, and Figure 22, effect of chlorine-to-nitrogen ratio on weight percent chlorine in product, help to show that a chlorine-hydrogen effect is operating. Figure 21 shows that API gravity decreases as hydrogen rate increases, and Figure 22 shows that as hydrogen rate increases the chlorine in the product increases. The last figure indicates that probably the chloride has not had sufficient time to diffuse to the catalyst surface and react at the higher hydrogen rates. It therefore remains unreacted and is found in the product.

Considering that both hydrogen and chloride diffusion may be a part of the overall denitrogenation mechanism, all subsequent runs were made at a hydrogen rate of 5000 SCF/bbl. This rate should be above the value Falk found to be hydrogen diffusion controlling and below the rate at which chlorine-hydrogen ratio dilution effects become important.

F. Effect of Temperature, Pressure, and Space Velocity on Nitrogen Removal

A series of runs was made to test the effects of temperature versus space velocity and pressure versus space velocity on nitrogen removal. The results of these runs are shown on Figures 23 and 26,

respectively. From Figure 23, effect of temperature and space velocity on nitrogen removal, it can be seen that the catalyst is active only over a relatively narrow range of temperatures. This range is from about 735 to 800°F. For these temperatures the percent nitrogen removal dropped 10 percent and an additional 20 percent when the temperature was lowered from 735 to 670°F; i.e., the rate of change of nitrogen removal with respect to temperature is higher at the lower temperatures than at the higher temperatures. This indicates that the last traces of nitrogen are harder to remove -- first, because the compounds containing the heterocyclic nitrogen are probably very stable and resistant to hydrogenation and hydrocracking; second, increasing temperature acts in such a way as to shift the thermodynamic equilibrium to a less favorable value (5,23). This change in activity with temperature is also a characteristic of the sulfide catalysts (22).

During the low temperature runs of this series, a large quantity of a very viscous material collected in the condenser and product collection flask. This material was identified as a quaternary ammonium salt (5) and indicates the hydrodenitrogenation reaction goes through a hydrochloride intermediate. This intermediate was probably stable enough at the lower temperatures to resist hydrocracking to a hydrocarbon and ammonium chloride, the major products of the runs made at 800°F.

The effect of pressure at a constant temperature of 800°F and various space velocities is shown in Figure 26. Pressure was varied between 800 and 1200 psig and space velocity was varied from 0.25 to 1.0 hr⁻¹. Nitrogen removal was increased with pressure over the whole pressure range and increased from about 74 and an estimated 92 percent at 800 psig to about 84 and 98 percent at 1200 psig for space velocities of 1.0 hr⁻¹ and 0.25 hr⁻¹, respectively. From the figure it appears that by increasing the pressure above 1200 psig, complete hydrodenitrogenation will occur. However, it has generally been noted that with heavy gas oils, complete hydrodenitrogenation is not easily obtained at pressures up to 6000 psig. Flinn (12) claims the reasons for this are that side reactions occur which yield nitrogen compounds in small amounts that are more difficult to hydrogenate than the original reactant. Also, the heterocyclic nitrogen-containing ring must be saturated during the reaction and the large groups that are attached to the ring appear to hinder this reaction (12).

Additional runs at lower temperatures could not be made because ammonium chloride plugged the system. Equipment limitations prevented temperatures higher than 800°F and pressures in excess of 1200 psig to be made.

G. Chlorine in Product Oil

All significant product samples were analyzed for chlorine since an organic chloride was blended with the feed oil.

Figure 22 relates the effect of percent cobalt on support, chlorine-nitrogen ratio, organic compound used, and hydrogen rate on weight percent chlorine in product. It appears that the means of adding the chloride using methylene, ethylene, or propylene chloride has no effect on the amount of chlorine in the product. This indicates that the organic chlorides are involved in reactions other than those involving impurity removal. McCandless noted that HCl could be a reaction product and that it might account for this observation.

Percent chlorine in the product was independent of the percent cobalt on support and was constant at about 0.4 percent chlorine for both alumina-silica supports used.

The effect of weight percent chlorine in product versus hydrogen rate has been discussed in a previous section -- Effect of Hydrogen Flow Rate on Nitrogen Removal.

Figures 29 and 30 show the effect of weight percent chlorine in product with temperature, pressure, and space velocity. At higher temperatures, a higher weight percent chlorine in the product was observed to occur at the higher space velocities. The opposite was observed at

lower temperatures. The change caused by temperature has been discussed and probably is the result of the formation of hydrochlorides that do not hydrocrack at the lower temperatures. At 800°F, the effect of space velocity is explained as a function of the hydrocracking reaction occurring. At the higher space velocities the residence time is low enough so that only a partial cracking of the hydrochloride takes place. Consequently, the fragmented hydrochloride not completely hydrocracked to ammonium chloride is soluble and remains in the product. At the low space velocities, residence time is long enough to cause a more complete hydrocracking to ammonium chloride and a hydrocarbon or hydrocarbons. At the low temperatures, the weight percent chlorine in the product was slightly dependent on space velocity. This indicated that the temperature was too low for a complete hydrocracking to occur at any of the space velocities studied.

The effect of pressure on weight percent chlorine is not well defined. The results shown on Figure 30 indicate that a decrease in product chlorine content occurs as pressure is increased. This is reasonable since impurity removal probably corresponds to an increase in the formation of ammonium chloride rather than a hydrochloride and hence a decrease in chlorine in the product.

H. Gas Production and Estimated Hydrogen Consumption

A quantitative determination of the major hydrocarbon gases in the effluent gas provided a method for determining the effect of changes in the various operating variables on hydrogen consumption. Hydrogen consumption is important because a plentiful supply of high pressure hydrogen is not readily available. Therefore, optimum use of the hydrogen is desired.

Table III gives the results of these determinations for most of the runs. Information is not available for the C- and AC-series because the procedure for chromatographic analysis was under development when these runs were made. The results of Run DC-6, a typical run in terms of hydrocarbon gas production, are: methane - 0.193; ethane - 0.0474; propane - 0.0552; iso-butane - 0.0251; and n-butane - 0.0220; with units of lb moles/bbl. The estimated hydrogen consumption for this run was 130.0 SCF/bbl oil.

The effect of chlorine-nitrogen ratio on estimated hydrogen consumption is shown in Figure 16. The trend is much the same as that of nitrogen removal versus chlorine-nitrogen ratio in that it increases from a low value -- 38 SCF/bbl -- to about 90 SCF/bbl at a chlorine-nitrogen ratio equal to 9.0. Above this value it increases more slowly as the chlorine-nitrogen ratio is increased. Although the rate of hydrogen consumption is a result of many competing reactions such as

hydrogenation, and hydrocracking (of the hydrogenated nitrogen and sulfur-containing compounds as well as other hydrocarbons in the feedstock), the hydrogen consumption followed closely the trend in impurity removed for changes in chlorine-nitrogen ratio.

Figures 19, 25, and 28 show the effect of hydrogen flow rate, temperature, pressure, and space velocity on the estimated hydrogen consumption. In all, the trend was the same as that observed with the chlorine-nitrogen ratio; i.e., as impurity removal decreases, hydrogen consumption decreases.

The results shown on Figure 25 warrant further discussion. Figure 25 shows the effect of temperature and space velocity on hydrogen consumption. At 800°F, the hydrogen consumption was very dependent on the space velocity and decreased substantially as the space velocity was increased. At the lower temperatures, hydrogen consumption was about independent of space velocity.

During the series of runs at 800°F, no significant quantity of heavy viscous products, thought to be hydrochlorides, was collected. However, at the lower temperatures a considerable quantity of the hydrochloride was found in the system. It is believed that these compounds formed by a chloride-nitrogen hydrogenation reaction at the metal sites on the catalyst, are not hydrocracked in a later step in the reaction because the hydrocracking reaction is slower at the reduced temperatures.

If no unsaturated hydrocarbons are produced when hydrocracking takes place, the hydrogen must react with the fragments to fill the valence of the available carbon atoms (or nitrogen atoms). No significant amount of unsaturated light hydrocarbons were observed in the effluent gas stream; i.e., only a trace of ethylene, no propylene or butenes were observed. Therefore, the reduced hydrogen consumption was probably directly related to the decrease in hydrocracking. The decrease in the production of the light hydrocarbon gases, normal reaction products of simple hydrocracking reactions, further established the trend of a decrease in the rate of hydrocracking at the lower temperatures.

Figure 19 shows the effect of hydrogen rate on hydrogen consumption. At the higher rates, less hydrogen per bbl of oil was consumed, indicating that the reaction rate of the many competing reactions involved was decreasing. This observation also verifies the observed decrease in nitrogen (and sulfur) removal with hydrogen rates exceeding 8000 SCF/bbl.

In general, the hydrogen consumptions reported in this investigation are in the range of those observed by industry. Reynolds (8) has reported that in treating a catalytic cracking feedstock, hydrogen consumption ranges from 20 to 250 SCF/bbl for operating conditions between 600 to 800°F, 650 to 3000 psig, LHSV equal to 1.0 hr⁻¹, and hydrogen treat rates of 350 to 1500 SCF/bbl. Under hydrocracking

conditions up to 1600 SCF H_2 /bbl was sometimes consumed (26). In this investigation, hydrogen consumption varied from 20 to 381 SCF/bbl for operating conditions between 670 to 800°F, 1000 to 12,000 psig, LHSV from 0.25 to 1.43 hr^{-1} , hydrogen rate of 5000 SCF/bbl, and a chlorine-nitrogen ratio of 9.0 atom/atom.

In order to compare the gas make and hydrogen consumption characteristics of the cobaltous chloride catalyst to those of a commercial catalyst, two runs were made using cobalt-molybdate as the catalyst. This catalyst was presulfided according to the method used by Falk (14). The operating conditions for these runs were identical to those with which they are compared. One of these runs, designated HC-3, when compared to Run DC-6 provided some interesting information. The amounts and ratios of the light hydrocarbon gases produced are of interest. A chromatograph trace of a gas sample analysis for these last two runs is shown on Figure 37. The gas make for these runs was: 0.1657 and 0.1930 lb moles/bbl methane; 0.0309 and 0.0474 lb moles/bbl ethane; 0.0319 and 0.0552 lb moles/bbl propane; 0.0160 and 0.0251 lb moles/bbl iso-butane; and 0.0124 and 0.0220 lb moles/bbl n-butane, for Runs HC-3 and DC-6, respectively. For Run HC-3, hydrogen consumption was 115.4 SCF/bbl and for Run DC-6 it was 130.0 SCF/bbl. From the chromatograph trace and the above data it is evident that since the ratio of iso- to n-butane has changed from less than one to greater than one, a change in the product distribution has occurred. Since iso-butane is of some-

what more value due to its use in refinery alkylation units, the product ratio from Run DC-6 is interesting.

The definite cause of this change in distribution is not known. It could be a result of isomerization or selective destructive hydrogenation caused by the highly acidic nature of the chloride system.

I. Comparison of Cobaltous Chloride to Other Catalysts

The activity of cobaltous chloride as a hydrodenitrogenation catalyst was compared to the activity of two other catalysts. The first was a commercial cobalt-molybdate catalyst which is representative of the most active commercial catalysts (14). The second is a laboratory-prepared nickelous-cobaltous chloride catalyst.

Figures 39 and 40 show the results of these comparisons. The operating conditions for these runs were: 800°F, 1000 psig, LHSV equal to 0.5 hr⁻¹, 5000 SCF H₂/bbl, and chlorine-nitrogen ratio equal to 9.0 atom/atom. The chloride, as methylene chloride, was added to the feed used for the chloride catalyst systems.

The first of these Figures shows that the cobaltous-chloride catalyst is somewhat more active for nitrogen removal than is Hourdy-C, the commercial catalyst. If based on percent conversions, the difference does not seem significant. However, if the results of the two Runs HC-2 and HC-3 are averaged and compared to Run CC-7, then, based on the nitrogen remaining in the product, a significant difference is

noted. The average product nitrogen concentration for the runs using the commercial catalyst is 280 ppm and for Run CC-7, 190 ppm. This difference is significant considering that it is very difficult to remove the last traces of nitrogen from a heavy feedstock.

The second of these Figures shows the comparison of the cobaltous chloride catalyst (Run CC-7) to a combined nickelous-cobaltous chloride catalyst (Run Ex-1). The Figure shows that the catalysts have essentially the same activity for denitrogenation. However, since little is known about the optimum combination of the nickel-cobalt chloride catalyst, it is probable that the ratio of the two metals is not optimum as is the percent cobalt in Run CC-7.

Mitchell (23) has pointed out that cobalt oxide (active as Co_9S_8) is not a good desulfurization catalyst by itself. Therefore, no comparison of cobalt oxide was made.

ASTM D-158 distillations were performed on the product from Run HC-3 (commercial catalyst) and Run DC-6 (cobaltous chloride) to determine if the type of catalyst used had a significant effect on the boiling point distribution of the product. Figure 38 shows that the average boiling point of the product from Run HC-3 was only slightly higher than that from Run DC-6. This indicates that the same degree of hydrocracking takes place in both systems. The ASTM D-158 distillation for the feed gas oil is also shown on the Figure.

J. Desulfurization

The catalysts that are presently used for hydrodenitrogenation were developed for hydrodesulfurization. In order to use them for denitrogenation, the reaction temperature and pressure used must be considerably higher than those required for desulfurization. Consequently, it has been found that when using the conventional catalyst for denitrogenation, if the nitrogen comes out the sulfur does, too (25).

Since the oil used in the hydrodenitrogenation studies contained 0.80 weight percent sulfur, most of the impurity removal trends were determined as a function of sulfur removal in addition to nitrogen removal. The results are somewhat surprising, considering the high hydrodenitrogenation activity obtained with the cobaltous chloride catalyst system.

In general, the sulfur removal followed the same trends as the nitrogen but at a lower percent removal. As can be seen from Figures 12 and 13, the optimum sulfur removal as a function of catalyst compositions is 65 percent at 3.5 percent cobalt for Harshaw 1802-E support and about 68 percent at 7.0 percent cobalt for Harshaw 1602-T. Again, as in nitrogen removal, Harshaw 1602-T proved to be a better support.

Figure 15 shows the effect of chlorine-nitrogen ratio and chloride carrier on sulfur removed. Increasing the chlorine-nitrogen ratio

above 9.0 did not change the sulfur removal significantly. In addition, the type of chloride carrier was not as important for sulfur removal as for nitrogen removal. This indicates that for the three organic compounds studied, all are identically reactive to the sulfur removal at the chlorine-nitrogen ratio used.

Sulfur removal increased at about the same rate with temperature changes as nitrogen but at a lower percent removal. Figure 24 shows that for a LHSV of 0.5 hr^{-1} , sulfur removal increased from about 48 percent at 670°F to 78 percent at 800°F . Again, it should be noted that there is an increase in the reported sulfur removal from the previous values of about 68 percent to 78 percent at identical operating conditions. This increase is due to the change in methods of preparing the reactor for each run.

Decreasing the space velocity is also shown to have an increasing effect on sulfur removal. See Figure 24.

As would be expected, sulfur removal was increased by increasing the reactor pressure. However, the increase was not very great, as shown in Figure 27. At a LHSV equal to 0.5 hr^{-1} , the sulfur removal increased from 76 to about 78 percent as pressure ranged from 800 to 1200 psig, respectively.

As previously stated, sulfur removal was generally quite low and at the optimum conditions it was about 86 percent. (Nitrogen removal at the same conditions -- 800°F, 1200 psig, 5000 SCF H₂/bbl, and chlorine-nitrogen ratio of 9.0 was 97 percent.) This is not too surprising considering that most sulfur compounds found in petroleum, i.e., thiophenes, etc., are acidic in nature and high desulfurization activity would not be expected using the highly acidic cobaltous chloride alumina-silica oxide catalyst.

K. Kinetics of Denitrogenation and Desulfurization

Levenspiel (27) states, "Chemical kinetics is simply the study of the factors that influence the rate of reaction and the explanations for the rate of reaction. For the chemical engineer the kinetics of a reaction must be known if he is to make a satisfactory design for equipment in which these reactions are to be effected on a technical scale." If the design engineer has kinetic correlations and reactor design equations available, he then has the tools necessary to determine how much time a reaction will require to produce a certain level of conversion. In this study a kinetic correlation is developed by fitting experimental data to a mathematical model describing the rate of reaction involving nitrogen and sulfur removal.

The determination of the rate equation is usually a two-step procedure involving an analytical analysis of experimental data. First, the concentration dependency, i.e., reaction order, is found

at a fixed temperature and then the temperature dependency of the rate constant is found.

There are two methods for analyzing kinetic data, the integral and the differential methods. In the integral analysis a kinetic model and rate equation are selected and after appropriate mathematical manipulations, one predicts that a plot of the concentration function versus time data should yield a straight line. If a straight line is obtained, the rate equation fits the data. In the differential method a kinetic model is selected and its corresponding rate expression fitted directly to the data. These methods provide a means of obtaining the concentration dependency of the proposed kinetic expression. The temperature dependency can then be found.

For many reactions the temperature dependent term, the reaction rate constant, has been found to be well represented by Arrhenius' Law (27). This law was used to describe the temperature dependency term of the denitrogenation and desulfurization rate expressions.

In order for the differential method of analysis to be useful, the data fitted must be extremely good or a large amount be available. In this study the data available is somewhat scarce. However, a good deal of information can be obtained by applying the differential analysis procedure to the data as an exploratory approach. Once the approximate concentration dependency of the rate equation is deter-

mined, by using the much easier differential analysis, the integral analysis can be applied to the same rate equation as a first approximation. This eliminates a considerable amount of time-consuming trial and error procedure.

As a basis for the kinetic analysis of the data, the following assumptions were made:

- 1) The reactants are in plug flow.
- 2) The hydrocarbon remains mainly in the liquid phase.
- 3) Hydrogen partial pressure and hence concentration is essentially constant through the reactor. This is accomplished by using an excess of hydrogen and maintaining the pressure in the reactor constant.
- 4) Chloride partial pressure and hence concentration is essentially constant. This is accomplished by using an excess over the stoichiometric amounts required for reaction.
- 5) Interaction between sulfur- and nitrogen-containing compounds is ignored.
- 6) The reaction is irreversible.

The proposed rate equation for this investigation as given for denitrogenation is:

$$(-r_N) = k'_N (N)^a (H)^b (Cl)^c$$

if (H) and (Cl) are in excess or their concentrations are such that small changes

do not affect the rate of reaction, then the rate equation can be written:

$$(-r_N) = k_N(N)^{a_N}$$

$$\text{where } k_N = k'_N (H)^{b'} (Cl)^{c'}$$

For desulfurization, the rate equation can be written by analogy as:

$$(-r_S) = k_S(S)^{a_S}$$

A plot of $\ln(r_N)$ versus $\ln(N)$ should yield a straight line with slope a_N , the pseudo order of the reaction.

Figures 31 and 34 show nitrogen and sulfur removal as a function of space time. The reaction rate of nitrogen removal was obtained from Figure 31 and plotted as a function of concentration as shown on Figure 32. The pseudo order of reaction for nitrogen removal was found to be 2.09. Because of the similarity in the shape of the curves for nitrogen and sulfur removal, the pseudo order of reaction for sulfur removal was assumed to be 2.0 for the application of integral analysis to the data.

A test for pseudo-second order reactions was made by plotting the integrated form of the rate equation. The rate equation can be

written, for nitrogen removal, as:

$$-\frac{dC_N}{dt} = k_N(C_N)^2$$

which, on integration, yields:

$$\frac{1}{C_N} - \frac{1}{C_{N_0}} = k_N t$$

Thus, a plot of $1/C_N$ versus t should yield a straight line if the proposed rate expression is correct and the pseudo order of reaction is correct. Figures 33 and 35, which test for the validity of this expression in terms of nitrogen and sulfur removal, show that the rate expression is valid. Consequently, 2 is the pseudo order of the reaction for both denitrogenation and desulfurization.

The temperature dependency was obtained using Arrhenius' Law:

$$k = k_0 e^{-E/RT}$$

$$\text{or} \quad \ln(k) = -(E/R)(1/T) + \ln(k_0)$$

Therefore, if $\ln(k)$ is plotted as a function of inverse temperature, the resulting straight line should have a slope equal to $-E/R$ and intercept k_0 . A plot of these values for this study is shown on Figure 36. The slope of the lines yields the activation energy, E , for each re-

action and is found to be 18.6 Kcal/g mole for both denitrogenation and desulfurization. The frequency factor, k_o , was found by the solution of Arrhenius' Law and is 7.66×10^7 for denitrogenation; 2.11×10^7 for desulfurization.

The design equation for plug flow reactors was used to evaluate the reaction rate constant, k , at each of the temperatures studied. This equation is:

$$\tau = \frac{1}{kC_{a0}^{a-1}} \int_{X_0}^X \frac{dX}{(1-X)^a} \quad (27)$$

and its development assumes a negligible change in volume between the reactants and products.

The final rate expressions are:

$$(-r_N) = 7.66 \times 10^7 e^{-18600/1.98T} (N)^2$$

for denitrogenation and:

$$(-r_S) = 2.11 \times 10^7 e^{-18600/1.98T} (S)^2$$

for desulfurization.

The nomenclature used in the above development is as follows:

$-r_N$	reaction rate for denitrogenation, (wt% N)(cc-oil)/(cc-catalyst)(hr)
$-r_S$	reaction rate for desulfurization, (wt% S)(cc-oil)/(cc-catalyst)(hr)
k_N	reaction rate constant for denitro- genation, (cc-oil)/(hr)(cc-catalyst)(wt% N)
k_S	reaction rate constant for desulfuri- zation, (cc-oil)/(hr)(cc-catalyst)(wt% S)
k_o	frequency factor, same units as k_N or k_S
(N)	nitrogen concentration, weight percent
(Cl)	chloride concentration
(S)	sulfur concentration, weight percent
(H)	hydrogen concentration
a_N, a_S	pseudo reaction order for denitrogen- ation and desulfurization
τ	space time, hrs
E	activation energy, cal/g mole
R	gas law constant, 1.98 cal/g mole $^{\circ}K$
T	temperature, $^{\circ}K$
X	conversion of nitrogen or sulfur
C_{a_o}	initial impurity concentration, weight percent

V. CATALYST LIFE CONSIDERATIONS

An important quality that all catalysts should possess is that they remain active over a long period of time. A long catalyst life is desired because of economic reasons which include down time as well as replacement or regeneration costs.

A long run (30 days) was made to test the life of the cobaltous catalyst. Because of the continued production of ammonium chloride as the major reaction product, it was made in a series of three ten-day runs. After ten days, the reactor was cooled, dismantled, cleaned and reassembled. The same catalyst was charged to the reactor each time it was cleaned. The operating conditions for this run were: 1000 psig, 800°F, LHSV equal to 0.5 hr^{-1} , 7500 SCF H_2/bbl , and a chlorine-nitrogen ratio of 9.0. The catalyst tested had 7.4% cobalt impregnated on Harshaw 1602-T support.

The results of this run are shown on Figure 41. As can be seen, the activity of the catalyst started off at about 85 percent removal and declined steadily to about 80 percent after nine days on stream. The rate of decline then slowed quite significantly and activity was almost constant for the remainder of the run.

Because of the low rate of deactivation from the ninth day on, the data from nine and one-half days to the end of the study were fitted, in the least square sense, to a first degree polynomial.

Table XIII gives the result of that fit and Figure 41 reflects the analysis of the data. The plot shows the best straight line through these data and has a slope of -0.0218 percent/day. At the end of the 30-day run, nitrogen removal was about 79 percent. The catalyst with which this run was made was not purged with hydrogen for 12 hours before contacting it with oil. Therefore, a shorter run was made to obtain information as to what effect this procedure might have on the life of the catalyst.

Figure 42 shows the results of this run. The operating variables were changed quite frequently to determine what effect this might have on the catalyst performance. As can be seen, the first change in operating variables occurred after about 40 hours on stream. At 80 hours, the original operating conditions were re-established. The net change in percent nitrogen removal was about 2.0 percent and probably was due to normal catalyst deactivation. Beginning at about 100 hours on stream, additional changes in operating were made over a 60-hour period. The original operating conditions were then re-established after 160 hours on stream with the effect of no net change in nitrogen removal. The final nitrogen removal was 87 percent at about 165 hours on stream.

The interpretation of these runs enables one to establish that the activity of the cobaltous chloride catalyst remains relatively high

for substantial periods of time. Since the deactivation of the catalyst is probably due largely to coke lay-down on the catalyst surface, anything that will lessen coke formation should lengthen the catalyst life. The major causes of coke formation are: 1) high temperatures -- hot spots are sometimes caused by channeling, 2) low hydrogen rates or partial pressures, and 3) the presence of high boiling fractions containing asphaltenes. Because of the last of these causes, the catalyst life studies using various feedstocks are difficult to compare unless accurate characterizations of the feedstocks are available. For this reason, no comparison with other catalyst life studies (5,14) was made.

VI. CONCLUSIONS

The primary objective of this investigation was to perform process development studies on the use of cobaltous chloride as a hydrodenitrogenation catalyst. In that capacity, the major conclusions of the study are presented.

- 1) Of the two alumina-silica catalyst supports investigated, Harshaw 1602-T proved to be best.
- 2) For maximum catalyst hydrodenitrogenation activity, a catalyst containing approximately 7.0 percent by weight cobalt is required if Harshaw 1602-T is used as the support.
- 3) The method used to prepare the catalyst allows the optimum use of the internal surface area of the catalyst.
- 4) To achieve the highest activity from the catalyst, the hot reactor and catalyst bed must be purged with hydrogen before contacting with oil. This procedure presumably removes all traces of moisture and air from the system. Some activation may also occur.
- 5) As expected, the developed catalyst's activity increased with increasing temperature and pres-

sure and decreased with increasing space velocity.

- 6) Methylene chloride was the best source of chloride necessary for catalyst activity. Increasing the chlorine-nitrogen ratio above 9.0 did not significantly increase the nitrogen removal.
- 7) For hydrogen treat rates between 2000 and 8000 SCF/bbl, no effect on nitrogen removal was noted. However, increasing the rate above 8000 SCF/bbl decreased the nitrogen removal, presumably because of chlorine-hydrogen ratio dilution effects.
- 8) Optimum reactor conditions for hydrodenitrogenation appeared to be:

Catalyst: 7.0 percent cobalt on Harshaw 1602-T
Temperature: greater than 750°F
Pressure: greater than 800 psig
Chlorine-nitrogen ratio: 9.0 atom/atom using
 methylene chloride
Hydrogen rate: greater than 4000 but less
 than 8000 SCF/bbl

Catalyst properties at temperatures greater than 800°F and pressures greater than 1200 psig were not studied.

- 9) The cobaltous chloride catalyst system was significantly better than a commercial cobalt molybdate catalyst because it reduced the product nitrogen

concentration from 280 to 190 ppm for runs performed at identical operating conditions. The boiling point distribution of product obtained from operating with both of these catalysts was nearly identical.

- 10) The trends in sulfur removal closely followed the trends in nitrogen removal but at a significantly lower percent conversion.
- 11) Both denitrogenation and desulfurization proceed under pseudo-second order reaction kinetics with respect to the impurity concentration.
- 12) A catalyst life study indicated that after a rapid deactivation over a 10-day period, percent nitrogen removal remained nearly constant for an additional 20 days. At the end of 30 days, 78.8 percent conversion was realized.

VII. RECOMMENDATIONS

The results of this investigation opened many avenues for further study on hydrodenitrogenation studies. The two which are felt to be of most importance are summarized here:

- 1) A detailed study concerning the mechanism by which the denitrogenation occurs would be useful in determining ways in which the catalyst performance might be improved. The ideas concerning certain points of a possible overall mechanism presented in this paper are strictly hypotheses concluded as a result of several meager observations. A detailed study to prove or disprove these ideas would have taken many years of study and deviated from the original intent of the research conducted.
- 2) The run made with a nickelous-cobaltous chloride catalyst opened the door for additional study of this system. Nickel types of catalyst are known to be very active but susceptible to poisoning while cobalt catalysts are considered to be rugged and resistant to poisoning. Therefore, an optimum nickel-cobalt catalyst might prove to have a longer useful life than either metal catalyst used separately.

VIII. APPENDIX

TABLE I. TEST OIL PROPERTIES.

Sample Designation	CR#5*	CR#8**
API Gravity 60°F/60°F	21.3	23.9
ASTM D-158***		
IBP	608	538
5%	656	585
10%	673	601
20%	693	623
30%	710	636
40%	724	646
50%	740	666
60%	752	672
70%	767	695
80%	777	712
90%		743
E.P.		760
Wt% Nitrogen	0.327	0.191
Wt% Sulfur	0.815	0.800

* Used only for Runs C-5 and C-9

** Used extensively in experimental work (see exception above)

*** Distillation at 640 mm corrected to 760 mm with
Sidney Young Equation

TABLE II. PROPERTIES OF COMMERCIAL CATALYSTS AND CATALYST SUPPORTS USED IN TESTS*

Catalyst Manufacturer: Houdry Process and Chemical Company

Identification Symbol: Houdry - C

Properties: 1/8" alumina extrusions

3.0% CoO

15.0% MoO₃

Surface Area: 310 to 340 m²/gr

Pore Volume: 0.45 cc/gr

Apparent Bulk Density: 53#/ft³

Average Pore Diameter: 55 Å

Catalyst Manufacturer: The Harshaw Chemical Company

Identification Symbol: Al-1802-E

Properties: 1/8" silicated high activity alumina extrusion

92% Al₂O₃

6% SiO₂

Surface Area: 277 m²/gr

Pore Volume: 0.91 cc/gr

Apparent Bulk Density: 33#/ft³

Average Pore Diameter: 132 Å

Catalyst Manufacturer: The Harshaw Chemical Company

Identification Symbol: Al-1602-T**

Properties: 1/8" silicated high activity alumina pellet

91% Al₂O₃

6% SiO₂

Surface Area: 210-240 m²/gr

Pore Volume: 0.48 cc/gr

Apparent Bulk Density: 52#/ft³

Average Pore Diameter: 91-80 Å

* Information supplied by manufacturer

** Support used extensively in investigation

TABLE III. EXPERIMENTAL DATA

Run Designation Code						
C, EX-series Exploratory						
AC-series Cobalt Concentration effect						
A1-series Harshaw Support only						
BC-series Chlorine Concentration and Carrier Effect						
CC-series Hydrogen Rate Effect						
DC-series Temperature-Space Velocity Effect						
EC-series Pressure Effect						
RUN NO.	C-5(a)	C-9(a)	A1-6	A1-7	AC-7	AC-9
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	5000	5000	7500	7500	7500	7500
5. Cl/N Ratio, atom/atom ^(b)	9.4	9.4	9.0	9.0	9.0	9.0
6. Catalyst, %Co ^(c)	6.0	7.2	0.0	0.0	5.4	8.8
7. Catalyst Support ^(d)	A	A	A	B	A	A
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	----	----	26.5	27.6	28.3	27.5
2. Wt% Nitrogen	0.032	0.026	0.067	0.042	0.035	0.039
3. Wt% Sulfur	----	----	0.396	0.342	0.291	0.272
4. Wt% Chlorine	----	----	0.252	0.264	0.435	0.347
C. Impurity Removal						
1. % Nitrogen	89.0	93.0	65.0	78.0	81.5	79.5
2. % Sulfur	----	----	50.5	57.3	63.6	66.5

(See NOTES on following page)

TABLE III (continued)

RUN NO.	AC-10	AC-11	AC-12	AC-13	AC-14	AC-15
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	7500	7500	7500	7500	7500	7500
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, %Co ^(c)	6.3	4.4	2.6	1.5	3.6	2.0
7. Catalyst Support ^(d)	A	A	A	A	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	----	27.1	----	27.5	26.3	27.9
2. Wt% Nitrogen	0.038	0.037	0.034	0.047	0.033	0.036
3. Wt% Sulfur	0.281	0.291	0.265	0.336	0.295	0.289
4. Wt% Chlorine	0.395	0.386	0.457	0.380	0.376	0.307
C. Impurity Removal						
1. % Nitrogen	80.0	80.5	82.0	75.0	83.0	81.0
2. % Sulfur	64.9	63.6	66.9	58.0	63.1	63.9

- NOTES: (a) Runs made using a Gas Oil Feed containing 0.327 Wt% Nitrogen.
 (b) Chlorine from methylene chloride unless otherwise noted.
 (c) If an asterisk, '*', appears after percent metal, the catalyst was purged with hydrogen for 12 hours before contacting with oil.
 " 'L' indicates that the catalyst was leached.
 (d) 'A' designates Harshaw 1802-E; 'B' designates Harshaw 1602-T.
 (e) Effluent Gas analysis not available for C and AC series runs.

TABLE III (continued)

RUN NO.	AC-16	AC-18	AC-19	AC-20	AC-21	AC-23
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	7500	7500	7500	7500	7500	7500
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, %Co ^(c)	6.0	2.9(L)	3.2	9.0	7.0	5.6(L)
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	----	28.3	27.6	27.7	28.0	28.0
2. Wt% Nitrogen	0.031	0.031	0.034	0.025	0.026	0.027
3. Wt% Sulfur	0.272	0.273	0.309	0.263	0.244	0.263
4. Wt% Chlorine	0.357	0.410	0.352	0.244	0.421	0.484
C. Impurity Removal						
1. % Nitrogen	84.0	84.0	82.0	87.0	86.5	86.0
2. % Sulfur	66.0	65.9	61.4	67.5	69.5	67.1

TABLE III (continued)

RUN NO.	AC-24	AC-26	AC-29	AC-30 ⁽¹⁾
A. Reactor Conditions				
1. Pressure, psig	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	7500	7500	7500	7500
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0
6. Catalyst, %Co ^(c)	7.1(L)	8.33	7.5(L)	7.2(L)
7. Catalyst Support ^(d)	B	B	B	B
B. Product Properties ^(e)				
1. API Gravity, 60°F/60°F	28.0	28.3	----	27.0
2. Wt% Nitrogen	0.029	0.027	0.027	0.040
3. Wt% Sulfur	0.252	0.251	0.278	----
4. Wt% Chlorine	0.387	0.476	0.299	----
C. Impurity Removal				
1. % Nitrogen	85.0	86.0	86.0	78.8
2. % Sulfur	68.5	68.6	65.5	----

NOTE: (1) Data taken at 29.5 days

TABLE III. (continued)

RUN NO.	BC-1	BC-2	BC-3	BC-4	BC-5	BC-6
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	7500	7500	7500	7500	7500	7500
5. Cl/N Ratio, atom/atom ^(b)	9	15	6	12	3	9 ⁽¹⁾
6. Catalyst, % Co ^(c)	7.0	7.0	7.0	7.0	7.0	7.0
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	27.8	28.5	27.6	27.9	27.5	27.7
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	143.6	151.2	115.5	131.7	69.5	63.7
b) Ethane	36.6	33.6	29.9	28.3	20.4	97.4
c) Propane	55.3	58.1	41.8	44.0	29.5	45.0
d) Iso-butane	32.7	41.4	19.6	27.5	11.7	25.6
e) N-butane	23.2	26.0	16.3	18.4	11.6	18.2
3. Estimated Hydrogen Consumption SCF/bbl oil	110.6	117.7	84.7	94.8	54.2	94.8
4. Wt% Nitrogen	0.031	0.021	0.036	0.027	0.047	0.042
5. Wt% Sulfur	0.294	0.236	0.293	0.253	0.353	0.260
6. Wt% Chlorine	0.467	0.509	0.442	0.527	0.354	0.527
C. Impurity Removal						
1. % Nitrogen	84.0	88.7	80.8	86.1	75.0	78.0
2. % Sulfur	63.4	70.5	63.4	68.4	58.9	67.5

NOTE: (1) CH₂ClCH₂Cl used to supply Cl.

TABLE III. (continued)

RUN NO.	BC-7	BC-8	BC-9	BC-10	CC-2	CC-3
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	7500	7500	7500	7500	8000	4000
5. Cl/N Ratio, atom/atom ^(b)	9.0 ⁽¹⁾	0.0	9.0	9.0 ⁽¹⁾	9.0	9.0
6. Catalyst, % Co ^(c)	7.0	7.0	7.0	7.0	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	27.7	26.5	----	28.1	28.4	31.4
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	56.9	47.3	220.6	102.6	100.9	189.6
b) Ethane	26.4	17.3	48.9	44.3	26.4	51.3
c) Propane	119.8	22.6	62.1	165.2	40.4	57.4
d) Iso-butane	21.6	6.5	34.7	28.3	24.4	28.2
e) N-butane	15.2	8.4	24.1	23.1	16.0	25.7
3. Estimated Hydrogen Consumption SCF/bbl oil	91.0	38.8	148.2	137.9	79.0	133.7
4. Wt% Nitrogen	0.042	0.063	0.025	0.040	0.017	0.014
5. Wt% Sulfur	0.274	0.374	----	0.255	0.262	0.181
6. Wt% Chlorine	0.452	0.240	----	0.450	0.337	0.221
C. Impurity Removal						
1. % Nitrogen	78.0	66.0	86.7	78.7	91.2	92.7
2. % Sulfur	65.7	53.3	----	67.8	67.3	76.8

NOTE: (1) CH₂ClCHClCH₃ used to supply Cl.

TABLE III (continued)

RUN NO.	CC-4	CC-6	CC-7	CC-8	CC-9	CC-10
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	6000	2000	7500	6000	10,000	12,000
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, % Co ^(c)	7.0*	7.0*	7.0*	7.0*	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	29.1	31.6	----	----	----	27.6
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	148.0	312.9	141.0	162.0	148.0	136.4
b) Ethane	36.7	73.8	33.7	43.9	36.8	30.7
c) Propane	46.4	28.9	47.4	57.5	55.4	45.0
d) Iso-butane	23.6	28.4	24.2	37.9	32.6	25.7
e) N-butane	19.5	25.5	18.3	25.3	21.7	16.0
3. Estimated Hydrogen Consumption SCF/bbl oil	104.1	178.2	100.4	124.0	112.0	96.6
4. Wt% Nitrogen	0.020	0.018	0.019	0.019	0.024	0.029
5. Wt% Sulfur	0.207	0.164	----	0.135	0.239	0.282
6. Wt% Chlorine	0.334	0.233	----	0.473	0.587	0.683
C. Impurity Removal						
1. % Nitrogen	89.7	90.5	90.2	90.2	87.6	85.0
2. % Sulfur	74.1	79.5	----	83.1	70.0	63.5

TABLE III (continued)

RUN NO.	CC-11	DC-1	DC-2	DC-3	DC-4	DC-5
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	1.0	1.43	0.25	0.67	2.0
4. Hydrogen Rate, SCF/bbl	4000	5000	5000	5000	5000	5000
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, % Co ^(c)	7.0*	7.0*	7.0*	7.0*	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	----	27.1	27.1	32.2	29.7	26.8
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	239.2	128.1	118.9	272.5	211.1	106.7
b) Ethane	65.2	25.2	26.5	74.4	49.0	22.9
c) Propane	74.6	32.3	31.6	86.3	59.7	24.5
d) Iso-butane	39.1	12.1	12.5	46.1	27.9	8.2
e) N-butane	32.6	10.8	12.9	35.7	27.9	9.1
3. Estimated Hydrogen Consumption SCF/bbl oil	171.0	79.1	76.8	195.4	142.5	65.1
4. Wt% Nitrogen	0.016	0.044	0.052	0.007	0.029	0.062
5. Wt% Sulfur	0.183	0.308	0.328	0.120	0.226	0.347
6. Wt% Chlorine	0.244	0.406	0.317	0.181	0.275	0.377
C. Impurity Removal						
1. % Nitrogen	91.6	77.2	72.7	96.1	84.7	67.8
2. % Sulfur	77.1	61.4	59.0	85.0	71.8	56.6

TABLE III (continued)

RUN NO.	DC-6	DC-7	DC-8	DC-9	DC-10	DC-11
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	800	735	735	735	735	735
3. LHSV, Hr ⁻¹	0.50	0.50	0.67	1.43	2.0	0.25
4. Hydrogen Rate, SCF/bbl	5000	5000	5000	5000	5000	5000
5. Cl/N Ratio, ^(b) atom/atom	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, % Co ^(c)	7.0*	7.0*	7.0*	7.0*	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	30.1	27.1	26.5	25.5	25.3	28.3
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	193.0	96.5	90.7	64.2	55.7	96.1
b) Ethane	47.4	15.0	11.5	5.9	6.7	18.7
c) Propane	55.2	21.5	15.4	8.5	9.2	28.1
d) Iso-butane	25.1	11.7	7.5	3.9	3.8	17.4
e) N-butane	22.0	8.6	5.9	3.6	3.5	11.7
3. Estimated Hydrogen Consumption SCF/bbl oil	130.0	58.2	49.7	32.6	30.0	65.3
4. Wt% Nitrogen	0.022	0.041	0.563	0.078	0.089	0.025
5. Wt% Sulfur	0.182	0.313	0.334	0.425	0.458	0.204
6. Wt% Chlorine	0.246	0.277	0.276	0.213	0.143	0.233
C. Impurity Removal						
1. % Nitrogen	88.6	78.6	70.5	59.4	53.2	87.1
2. % Sulfur	77.2	60.9	58.3	46.9	42.7	74.5

TABLE III (continued)

RUN NO.	DC-12	DC-13	DC-14	DC-15	DC-16	DC-17
A. Reactor Conditions						
1. Pressure, psig	1000	1000	1000	1000	1000	1000
2. Temperature, °F	735	670	670	670	670	670
3. LHSV, Hr ⁻¹	1.0	0.50	1.43	1.0	0.25	0.67
4. Hydrogen Rate, SCF/bbl	5000	5000	5000	5000	5000	5000
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0	9.0
6. Catalyst, % Co ^(c)	7.0*	7.0*	7.0*	7.0*	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B	B
B. Product Properties ^(e)						
1. API Gravity, 60°F/60°F	26.1	25.3	24.8	24.7	25.7	25.2
2. Gas Production lb moles/bbl oil x 10 ³						
a) Methane	64.9	64.0	44.3	49.7	93.3	75.3
b) Ethane	8.1	3.9	1.8	2.2	8.4	4.7
c) Propane	11.3	5.1	4.8	4.3	10.9	6.2
d) Iso-butane	4.9	2.2	1.1	1.4	5.7	2.9
e) N-butane	4.1	1.8	0.9	1.2	5.3	2.4
3. Estimated Hydrogen Consumption SCF/bbl oil	35.4	29.2	20.1	22.4	46.9	34.7
4. Wt% Nitrogen	0.068	0.078	0.115	0.104	0.064	0.095
5. Wt% Sulfur	0.381	0.469	0.580	0.557	0.414	0.503
6. Wt% Chlorine	0.215	0.128	0.081	0.085	0.081	0.888
C. Impurity Removal						
1. % Nitrogen	64.5	59.0	39.8	45.5	66.6	50.3
2. % Sulfur	52.4	41.4	27.5	30.4	48.3	37.1

TABLE III (continued)

RUN NO.	EC-2	EC-3	EC-4	EC-5	EC-6
A. Reactor Conditions					
1. Pressure, psig	1200	1200	1200	800	800
2. Temperature, °F	800	800	800	800	800
3. LHSV, Hr ⁻¹	0.5	1.0	0.25	0.5	1.00
4. Hydrogen Rate, SCF/bbl	5000	5000	5000	5000	5000
5. Cl/N Ratio, atom/atom ^(b)	9.0	9.0	9.0	9.0	9.0
6. Catalyst, % Co ^(c)	7.0*	7.0*	7.0*	7.0*	7.0*
7. Catalyst Support ^(d)	B	B	B	B	B
B. Product Properties ^(e)					
1. API Gravity, 60°F/60°F	30.8	28.6	35.3	29.5	27.1
2. Gas Production lb moles/bbl oil x 10 ³					
a) Methane	164.8	113.4	528.0	186.1	141.7
b) Ethane	45.6	27.9	138.9	51.9	34.6
c) Propane	71.3	43.4	169.6	73.0	44.7
d) Iso-butane	53.0	24.0	110.1	47.5	26.4
e) N-butane	30.3	17.1	53.3	27.9	15.3
3. Estimated Hydrogen Consumption SCF/bbl oil	138.4	85.7	381.4	146.7	99.8
4. Wt% Nitrogen	0.009	0.027	0.006	0.031	0.049
5. Wt% Sulfur	0.154	0.266	0.093	0.192	0.320
C. Impurity Removal					
1. % Nitrogen	95.5	86.1	96.8	84.2	74.4
2. % Sulfur	80.1	66.1	88.4	76.0	60.0

TABLE III (continued)

RUN NO.	HC-2	HC-3	EX-1
A. Reactor Conditions			
1. Pressure, psig	1000	1000	1000
2. Temperature, °F	800	800	800
3. LHSV, Hr ⁻¹	0.5	0.5	0.5
4. Hydrogen Rate, SCF/bbl	5000	5000	5000
5. Cl/N Ratio, (b) atom/atom	----	----	9.0
6. Catalyst, % Co (c)	(1)	(1)	(2)
7. Catalyst Support (d)	----	----	B
B. Product Properties(e)			
1. API Gravity, 60°F/60°F	----	30.2	30.7
2. Gas Production lb moles/bbl oil x 10 ³			
a) Methane	----	167.5	165.7
b) Ethane	----	59.7	30.9
c) Propane	----	45.8	31.9
d) Iso-butane	----	7.2	16.0
e) N-butane	----	23.9	12.4
3. Estimated Hydrogen Consumption SCF/bbl oil	----	115.4	97.5
4. Wt% Nitrogen	0.031	0.025	0.0174
5. Wt% Sulfur	----	----	----
6. Wt% Chlorine	----	----	----
C. Impurity Removal			
1. % Nitrogen	84.0	87.5	91.0
2. % Sulfur	----	----	----

NOTE: (1) Houdry-C Catalyst; (2) 3.8% Co; 3.8% Ni

TABLE IV. FORTRAN II COMPUTER PROGRAM FOR CURVE FITTING USED IN LIFE STUDY ANALYSIS AND GAS CHROMATOGRAPH CALIBRATION ANALYSIS.

*LIST PRINTER

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```
C      POLYNOMIAL CURVE FIT -MAXIMUM DEGREE IS 10
C      WILL FIT FOUR TYPES OF CURVES  TYPE NUMBERS ARE BELOW
C      1 IS YVSX, 2 IS LOGYVSX, 3 IS LOGYVSLOGX, 4 IS YVSLOGX
C      DIMENSION X(100),Y(100),C(11), A(11,12)
C      READ IN POLYNOMIAL DATA
C      COMMON X,Y,N,IM,C,IY
73 DO 27 M=1,100
    READ 901, WX,WY
    IF(WX + .1E+04) 9,33,10
10  Y(M) = WY
    X(M) = WX
27  CONTINUE
    9 N=M-1
C      READ DESIRED DEGREE AND TYPE
1000 READ 900, ITYPE,IDEG
    IF(ITYPE) 41,41,40
40  PRINT 906,ITYPE,IDEG
    PRINT 907
    IM=IDEG+1
    IY=IM+1
C      SET MATRIX A(I,J)=0.0
    DO 1 I=1,IM
    DO 1 J=1,IY
1  A(I,J)=0.0
C      GENERATE POLYNOMIAL COEFFICIENTS
    DO 2 K=1,N
    WX = X(K)
    WY = Y(K)
    GO TO (4,4,3,3),ITYPE
3  WX=LOGF(WX)
4  GO TO (6,5,5,6),ITYPE
5  WY=LOGF(WY)
6  W=1.0
    DO 7 I=1,IM
    A(1,I)=A(1,I)+W
    A(I,IM+1)=A(I,IY)+WY
    W=W*WX
7  WY=WY*WX
```

TABLE IV (continued)

DAVID WHITCOMB

```

      DO 8 I=2,IM
      A(I,IM)=A(I,IM)+W
      8 W=W*WX
      2 CONTINUE
      IF(IDEG-1) 20,20,30
30 DO 11 I=2,IDEG
      DO 11 J=I, IDEG
11 A(I,J)=A(I-1,J+1)
20 DO 12 I=2,IM
      DO 12 J=I,IY
      DO 12 K=2,I
12 A(I,J)=A(I,J)-A(K-1,I)*A(K-1,J)/A(K-1,K-1)
      C(IM)=A(IM,IY)/A(IM,IM)
      PRINT 902,IDEG,C(IM)
      DO 14 I=2,IM
      K=IY-I
      W=A(K,IY)
      DO 13 J=2,I
      L=IM+2-J
13 W=W-C(L)*A(K,L)
      C(K)=W/A(K,K)
      M=K-1
14 PRINT 902,M,C(K)
      PRINT 903
      SUMSQ=0.0
C   CALCULATE AND PRINT VALUES AND ERROR AT EACH POINT
      DO 15 K=1,N
      W=X(K)
      GO TO (17,17,16,16),ITYPE
16 W=LOGF(W)
17 YC=0.0
      DO 18 I=1,IM
      J=IY-I
18 YC=YC*W+C(J)
      GO TO (21,19,19,21),ITYPE
19 YC=EXPF(YC)
21 YEA=Y(K)-YC
      SUMSQ=SUMSQ+YEA*YEA
      PRINT 905,X(K),Y(K),YC,YEA
15 CONTINUE
      PRINT 908,SUMSQ
      PAUSE

```

TABLE IV . (continued)

DAVID WHITCOMB

```
      CALL WPL0T1
      GO TO 1000
41  CONTINUE
      GO TO 73
33  CONTINUE
900  FORMAT(2I2)
901  FORMAT(2F10.6)
902  FORMAT(3H C(,I2,1H),E14.8)
903  FORMAT(//9X1HX,14X,1HY,11X,6HY CALC,8X,9HABS ERROR,/)
905  FORMAT(4F15.6)
906  FORMAT( 6H11TYPE,I3,4X,7H DEGREE,I3,/)
907  FORMAT(42H COEFFICIENTS OF POLYNOMIAL FITTED TO DATA,
110H ARE BELOW/)
908  FORMAT(//27H SUM OF SQUARES OF ERRORS =,E14.8/)
      CALL EXIT
      END
```

TABLE V. FORTRAN II COMPUTER SUBROUTINE USED TO PLOT GAS CHROMATOGRAPH CALIBRATION CURVES.

*LIST PRINTER

** DAVID WHITCOMB 110-67

*LDISKWPLOT1

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```

SUBROUTINEWPL0T1
DIMENSION X(100),Y(100),C(11)
COMMON X,Y,N,IM,C,IY
C   XMAX IS THE MAXIMUM PEAK HEIGHT
C   YMAX IS THE MAXIMUM COCENTRATION
C   XXMAX IS THE MAXIMUM PEAK HEIGHT
C   ON PLOT YYMAX IS THE MAXIMUM
C   CONCENTRATION ON PLOT
READ 20, XMAX,YMAX,XD,YD,XXMAX,YYMAX
XL=4.0
YL=2.5
XMIN=0.0
YMIN=0.0
XS=(XXMAX-XMIN)/XL
YS=(YYMAX-YMIN)/YL
CALL PLOT(1,XMIN,XXMAX,XL,XD,YMIN,YYMAX,YL,YD)
CALL PLOT(99)
DO 10 I=1,N
CALL PLOT(9,X(I),Y(I))
10 CALL PLOTSY(X(I),Y(I),0.1,XS,YS,4)
CALL PLOT(99)
C   K IS THE NUMBER OF POINTS CALCULATED AND PLOTTED
K=50
WK=K
WWK = (XMAX - XMIN)/WK
X0=0.
DO 11 KK=1,K
W=XMIN+X0
X0 = X0 + WWK
YC=0.0
DO 12 I=1,IM
J=IY-I
12 YC=YC*W+C(J)
11 CALL PLOT(0,W,YC)
CALL PLOT(99)
CALL PLOT(7)
20 FORMAT (6F10.0)

```

TABLE V (continued)

DAVID WHITCOMB 110-67

RETURN

END

TABLE VI. FORTRAN II COMPUTER PROGRAM FOR DETERMINATION OF GAS PRODUCTION FROM EFFLUENT GAS ANALYSIS USING FITTED CALIBRATION CURVE.

*LIST PRINTER

** DAVID WHITCOMB

DAVID WHITCOMB

```

C      PROGRAM FOR DETERMINATION OF GAS PRODUCTION AT STP
C      STANDARD CONDITIONS ARE 760MM HG, 60DEG F
C      ON SECOND DATA CARD POSTION RUN NO IN COLUMNS 2 TO 9
C      LEGEND 1=METHANE 2=ETHANE 3=PROPANE 4=ISO-BUTANE
C      5=N-BUTANE ***SIZE=INJECTION SAMPLE SIZE IN CC***
C      DIMENSION P(5),GMOLE(5),SCF(5),GLBM(5)
10 READ 2, TEMP,PRESS,OLHSV,H2RATE,CLN
    IF(TEMP) 20,21,21
21 READ 1
    READ 2,(P(I),I=1,5)
    READ 3, BAROM,AMBTM,SIZE
    ABST=460.+AMBTM
    CORR=(BAROM*537.)/(635.*ABST)*(1./SIZE)
    GMOLE(1)=(.2865E-06*P(1)**3-.1021E-04*P(1)**2+
1.1027E-01*P(1)-.1750E-06)*CORR
    GMOLE(2)=(.7512E-07*P(2)**3+.2225E-04*P(2)**2+
1.5455E-02*P(2)-.2500E-06)*CORR
    GMOLE(3)=(.1382E-07*P(3)**3+.3974E-05*P(3)**2+
1.3741E-02*P(3)+.5250E-06)*CORR
    GMOLE(4)=(.3658E-08*P(4)**3+.3436E-05*P(4)**2+
1.2643E-02*P(4)-.5000E-07)*CORR
    GMOLE(5)=(-.5157E-08*P(5)**4+.6722E-06*P(5)**3-
1.1677E-04*P(5)**2+.3721E-02*P(5)+.6500E-07)*CORR
    FT3LBM=359.*520./492.
    SMOLE=0.0
    DO 12 I=1,5
12 SMOLE=SMOLE + GMOLE(I)
    ESTH=SMOLE*H2RATE /100.
    HMOLE=100.0-SMOLE
    DO 13 I=1,5
    SCF(I)=H2RATE*GMOLE(I)/100.
13 GLBM(I)=SCF(I)/FT3LBM
    PRINT 4
    PRINT 5
    PRINT 1, TEMP,PRESS,OLHSV,H2RATE,CLN
    PRINT 6
    DO 14 I=1,5
14 PRINT 7, I,GLBM(I),GMOLE(I)

```

TABLE VI (continued)

DAVID WHITCOMB

```
      PRINT 9,          HMOLE
      PRINT 8, ESTH
      GO TO 10
20 CONTINUE
  1 FORMAT(10H          , F8.2,2X,F8.0,2X,F7.2,3X,F8.0,
    1F8.1)
  2 FORMAT(5F10.2)
  3 FORMAT(3F10.2)
  4 FORMAT(21H1OPERATING CONDITIONS)
  5 FORMAT(/ /8H RUN    ,2X,10H TEMP    ,10H PRESSURE ,
    110H LHSV.    ,10H H2RATE    ,10H CLN    )
  6 FORMAT(/ /27H MOLES GAS PRODUCED PER BBL,3X,
    130HPERCENT GAS IN EFFLUENT STREAM)
  7 FORMAT(10H COMPONENT,I3,3X,F10.6,19X,F10.6)
  8 FORMAT(/ /31H ESTIMATED HYDROGEN CONSUMPTION,F10.3,
    113HSCFH2/BBL OIL)
  9 FORMAT(3X,9H HYDROGEN,33X,F10.6)
      CALL EXIT
      END
```

TABLE VII. GAS CHROMATOGRAPH CALIBRATION CURVE DATA FOR METHANE.

ITYPE 1 DEGREE 3

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(3) .28654711E-06
C(2) -.10208557E-04
C(1) .10266258E-01
C(0) -.17500000E-06

X	Y	Y CALC	ABS ERROR
0.000000	0.000000	0.000000	0.000000
71.000000	.780000	.780001	-.000001
119.000000	1.560000	1.559998	.000001
178.000000	3.120000	3.120000	0.000000

SUM OF SQUARES OF ERRORS = .34502250E-11

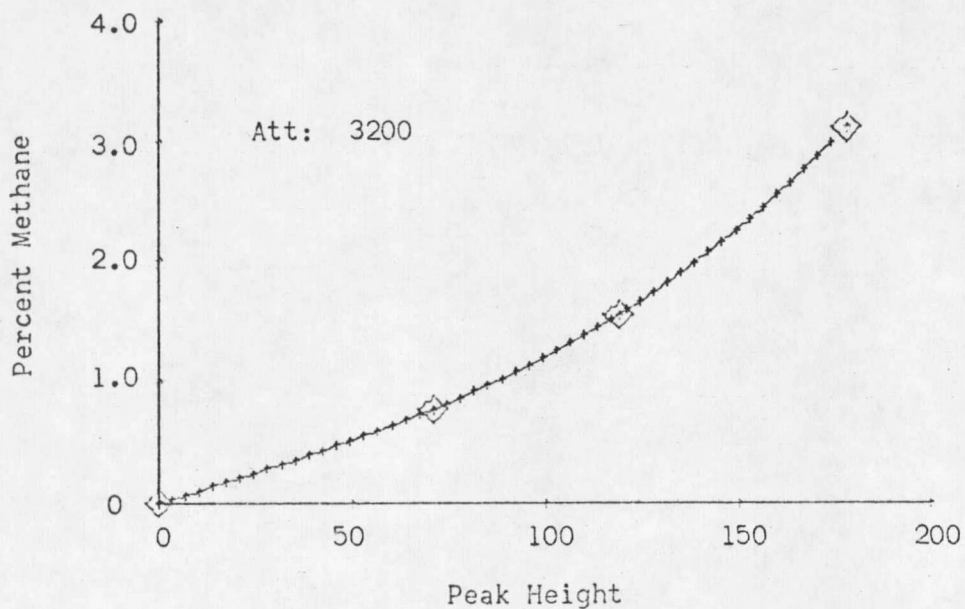


Figure 2. Methane Calibration Curve.

TABLE VIII. GAS CHROMATOGRAPH CALIBRATION CURVE DATA FOR ETHANE.

ITYPE 1 DEGREE 3

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(3) .75118176E-07
C(2) .22246999E-04
C(1) .54549601E-02
C(0) -.25000000E-06

X	Y	Y CALC	ABS ERROR
0.000000	0.000000	0.000000	0.000000
61.600000	.438000	.438001	-.000001
102.600000	.875000	.874998	.000001
160.000000	1.750000	1.750000	0.000000

SUM OF SQUARES OF ERRORS = .44651000E-11

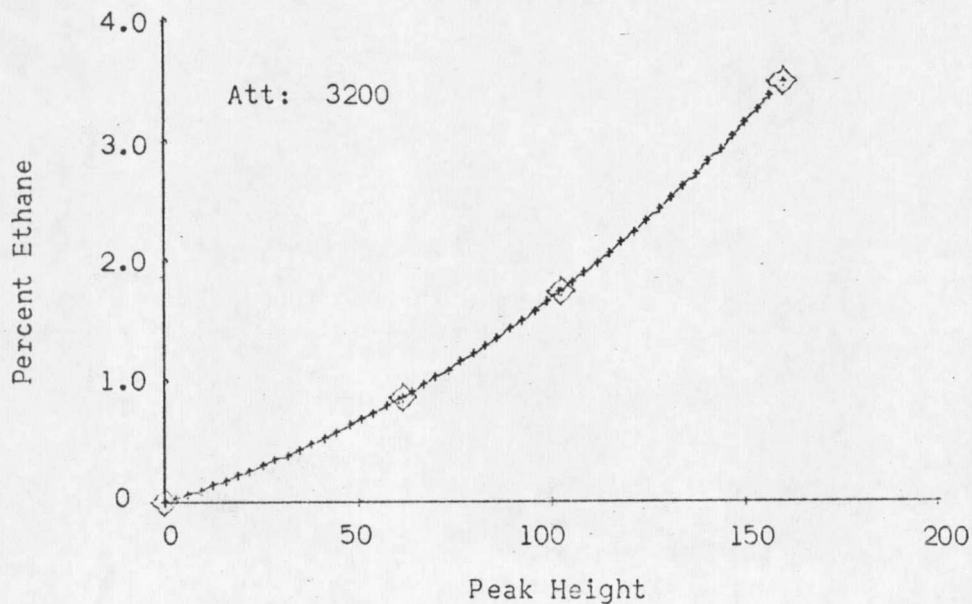


Figure 3. Ethane Calibration Curve.

TABLE IX. GAS CHROMATOGRAPH CALIBRATION CURVE DATA FOR PROPANE.

ITYPE 1 DEGREE 3

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(3) .13816971E-07
C(2) .39739291E-05
C(1) .37408868E-02
C(0) .52500000E-06

X	Y	Y CALC	ABS ERROR
0.000000	0.000000	0.000000	0.000000
76.800000	.317000	.316998	.000001
139.200000	.635000	.635000	0.000000
234.000000	1.270000	1.269999	0.000000

SUM OF SQUARES OF ERRORS = .27676250E-11

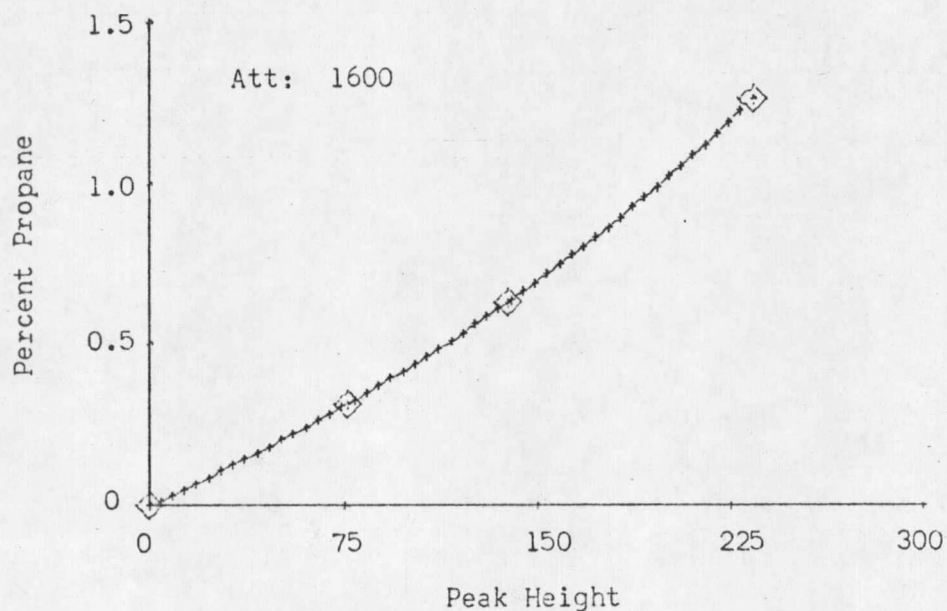


Figure 4. Propane Calibration Curve.

TABLE X. GAS CHROMATOGRAPH CALIBRATION CURVE DATA FOR ISO-BUTANE.

ITYPE 1 DEGREE 3

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(3) .36582592E-08
C(2) .34356961E-05
C(1) .26429655E-02
C(0) -.50000000E-07

X	Y	Y CALC	ABS ERROR
0.000000	0.000000	0.000000	0.000000
100.200000	.303000	.302999	0.000000
179.200000	.605000	.605000	0.000000
301.600000	1.210000	1.209999	0.000000

SUM OF SQUARES OF ERRORS = .20380000E-12

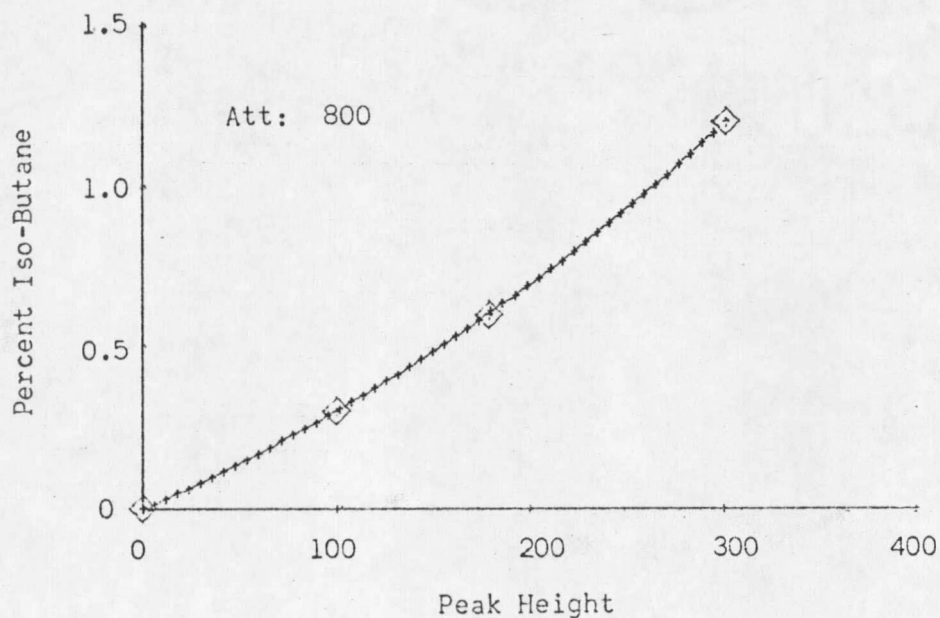


Figure 5. iso-Butane Calibration Curve.

TABLE XI. GAS CHROMATOGRAPH CALIBRATION CURVE DATA FOR N-BUTANE

ITYPE 1 DEGREE 4

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(4) -.51570647E-08
 C(3) .67219377E-06
 C(2) -.16770167E-04
 C(1) .37208348E-02
 C(0) .65000000E-07

X	Y	Y CALC	ABS ERROR
0.000000	0.000000	0.000000	0.000000
20.200000	.073000	.072999	0.000000
38.400000	.145000	.145000	0.000000
71.200000	.290000	.289999	0.000000

SUM OF SQUARES OF ERRORS = .18106000E-13

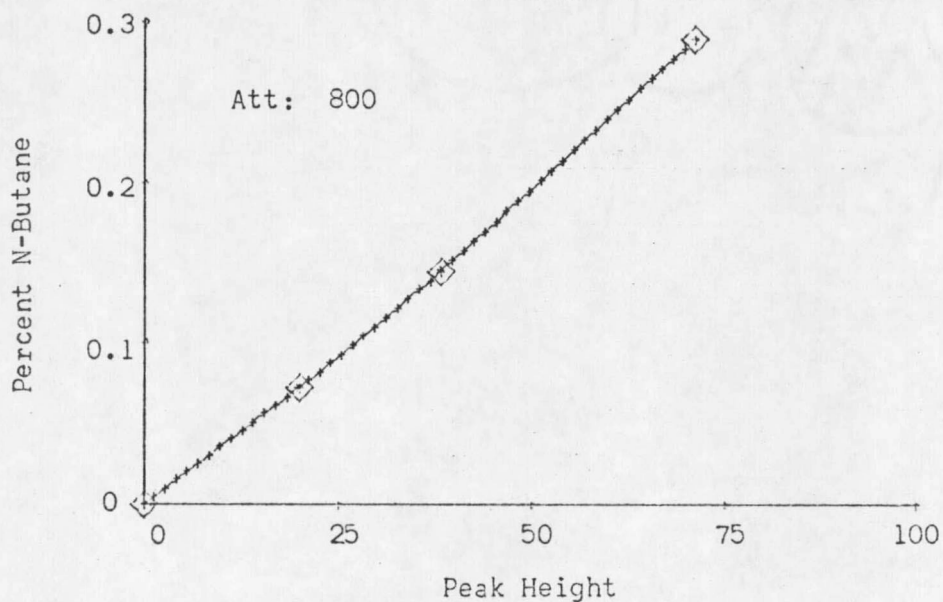


Figure 6. n-Butane Calibration Curve.

TABLE XII. TYPICAL OUTPUT DATA FROM FORTRAN II PROGRAM -- DETERMINATION OF GAS PRODUCTION.

OPERATING CONDITIONS

RUN	TEMP	PRESSURE	LHSV	H2RATE	CLN
DC-6-2	800.00	1000.	.50	5000.	9.0

MOLES GAS PRODUCED PER BBL		PERCENT GAS IN EFFLUENT STREAM
COMPONENT 1	.193038	1.464897
COMPONENT 2	.047391	.359632
COMPONENT 3	.055213	.418993
COMPONENT 4	.025049	.190089
COMPONENT 5	.022039	.167248
HYDROGEN		97.399140

ESTIMATED HYDROGEN CONSUMPTION 130.043SCFH2/BBL OIL

TABLE XIII. DATA FOR LEAST SQUARES FIRST DEGREE FIT OF LIFE STUDY
DATA FROM NINE AND ONE-HALF DAYS TO END.

ITYPE 1 DEGREE 1

COEFFICIENTS OF POLYNOMIAL FITTED TO DATA ARE BELOW

C(1) -.21812979E-01

C(0) .79522889E+02

X	Y	Y CALC	ABS ERROR
9.416666	78.000000	79.317484	-1.317484
9.958333	78.000000	79.305669	-1.305669
10.416666	80.000000	79.295671	.704329
10.958333	79.100000	79.283856	-.183856
11.416666	80.700000	79.273858	1.426142
11.937500	75.700000	79.262497	-3.562497
12.500000	80.000000	79.250227	.749773
13.000000	79.800000	79.239321	.560679
13.437500	78.000000	79.229778	-1.229778
13.937500	80.200000	79.218871	.981129
14.416666	79.400000	79.208419	.191581
14.975000	81.200000	79.196240	2.003760
15.583333	78.000000	79.182971	-1.182971
16.062500	79.900000	79.172519	.727481
16.562500	79.000000	79.161612	-.161612
16.979166	78.200000	79.152523	-.952523
17.479166	79.300000	79.141617	.158383
17.916666	79.300000	79.132074	.167926
18.541666	79.300000	79.118441	.181559
19.708333	81.700000	79.092992	2.607008
20.270833	80.500000	79.080722	1.419278
20.750000	78.100000	79.070270	-.970270
21.229166	81.700000	79.059818	2.640182
21.770833	80.000000	79.048003	.951997
22.229166	79.000000	79.038005	-.038005
22.770833	78.500000	79.026190	-.526190
23.229166	80.300000	79.016192	1.283808
23.833333	77.500000	79.003014	-1.503014
24.270833	79.200000	78.993470	.206530
25.270833	77.200000	78.971657	-1.771657
25.770833	79.000000	78.960751	.039249
26.270833	78.500000	78.949844	-.449844

TABLE XIII (continued)

26.729166	78.500000	78.939847	-.439847
27.270833	79.200000	78.928031	.271969
27.770833	78.200000	78.917125	-.717125
28.270833	77.200000	78.906218	-1.706218
28.729166	79.800000	78.896221	.903779
29.270833	78.800000	78.884405	-.084405
29.770833	78.800000	78.873499	-.073499

SUM OF SQUARES OF ERRORS = .58769433E+02

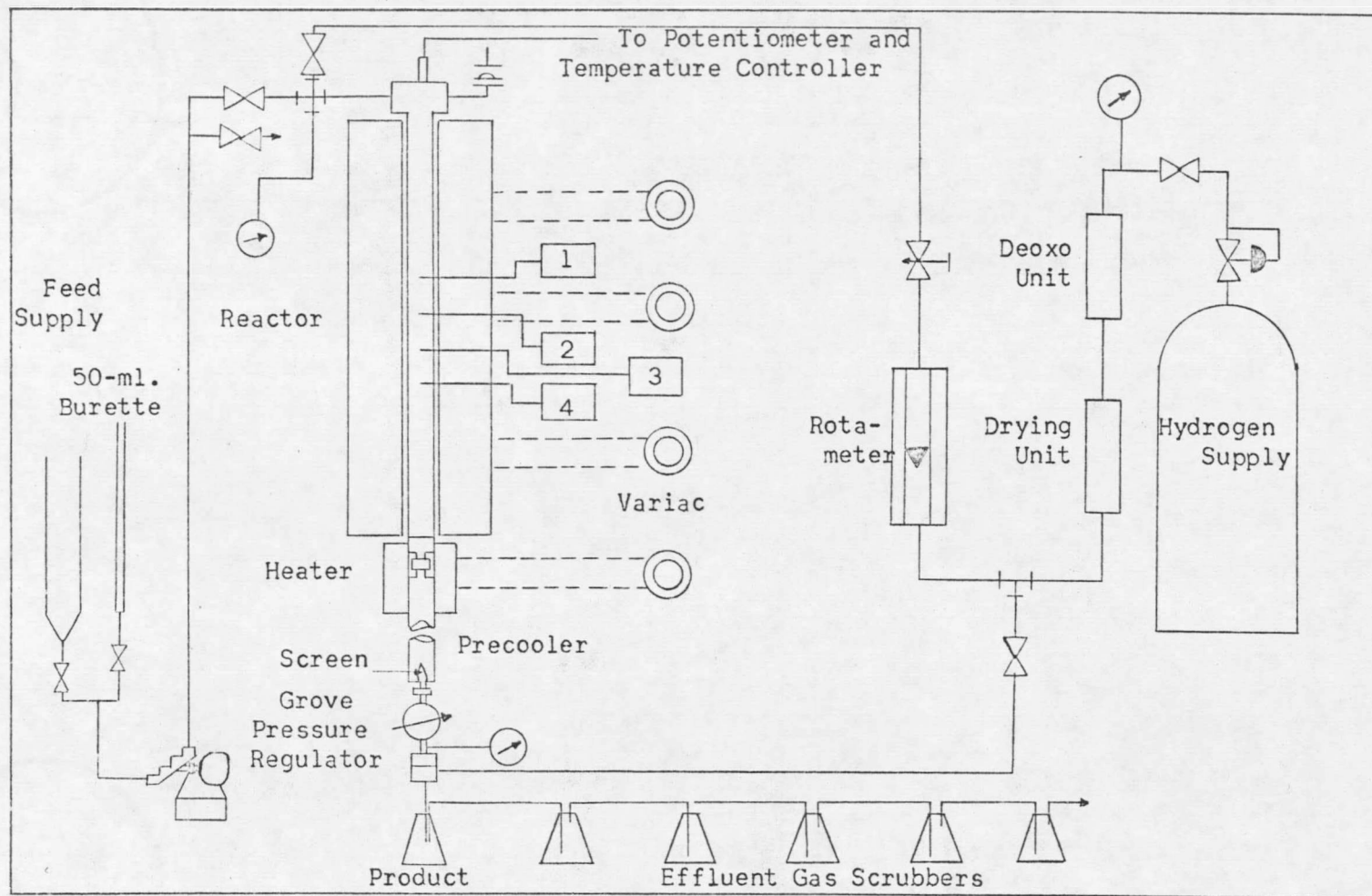


Figure 7. Schematic Flow Diagram of Reactor System.

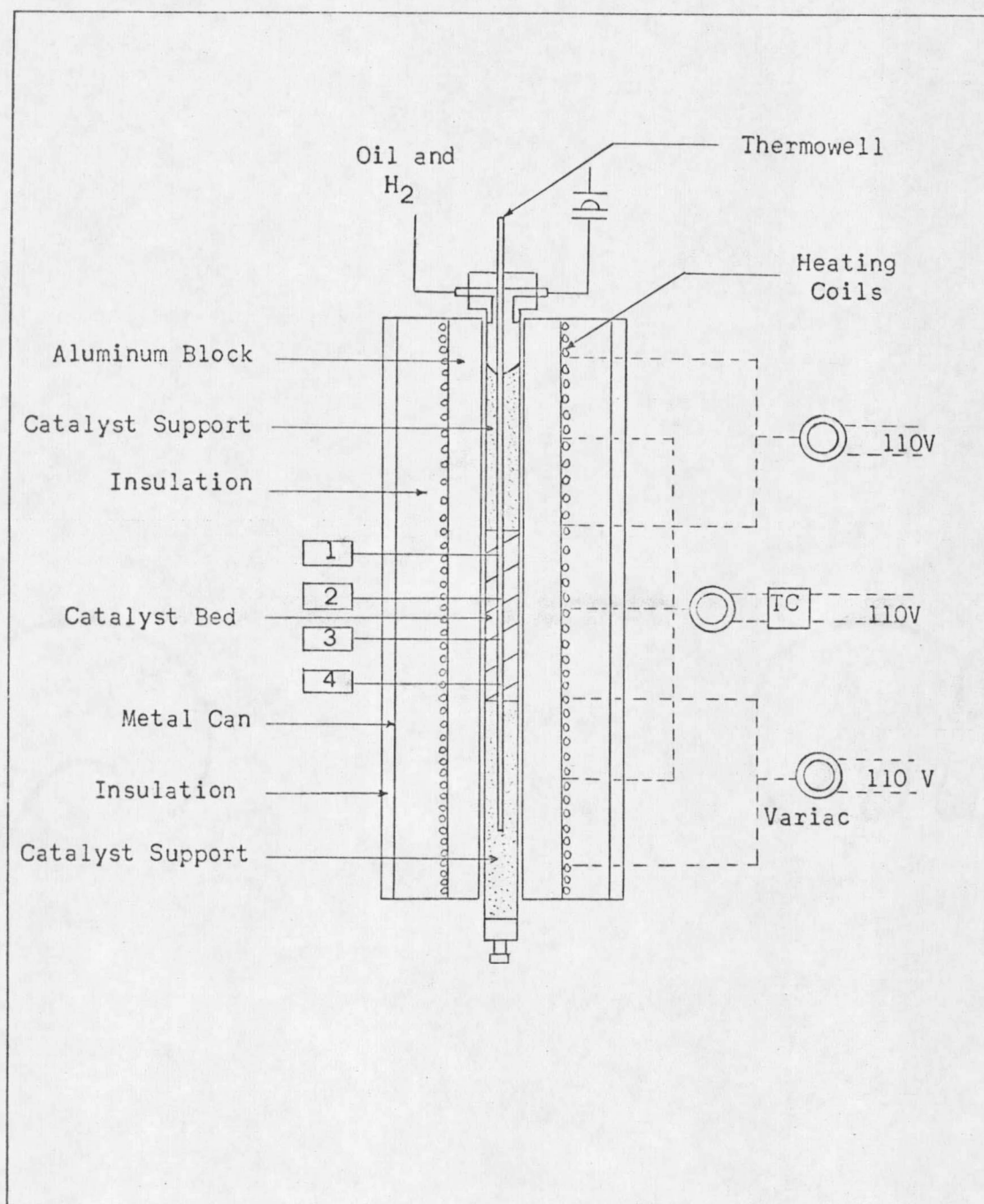


Figure 8. Detailed Diagram of Reactor.

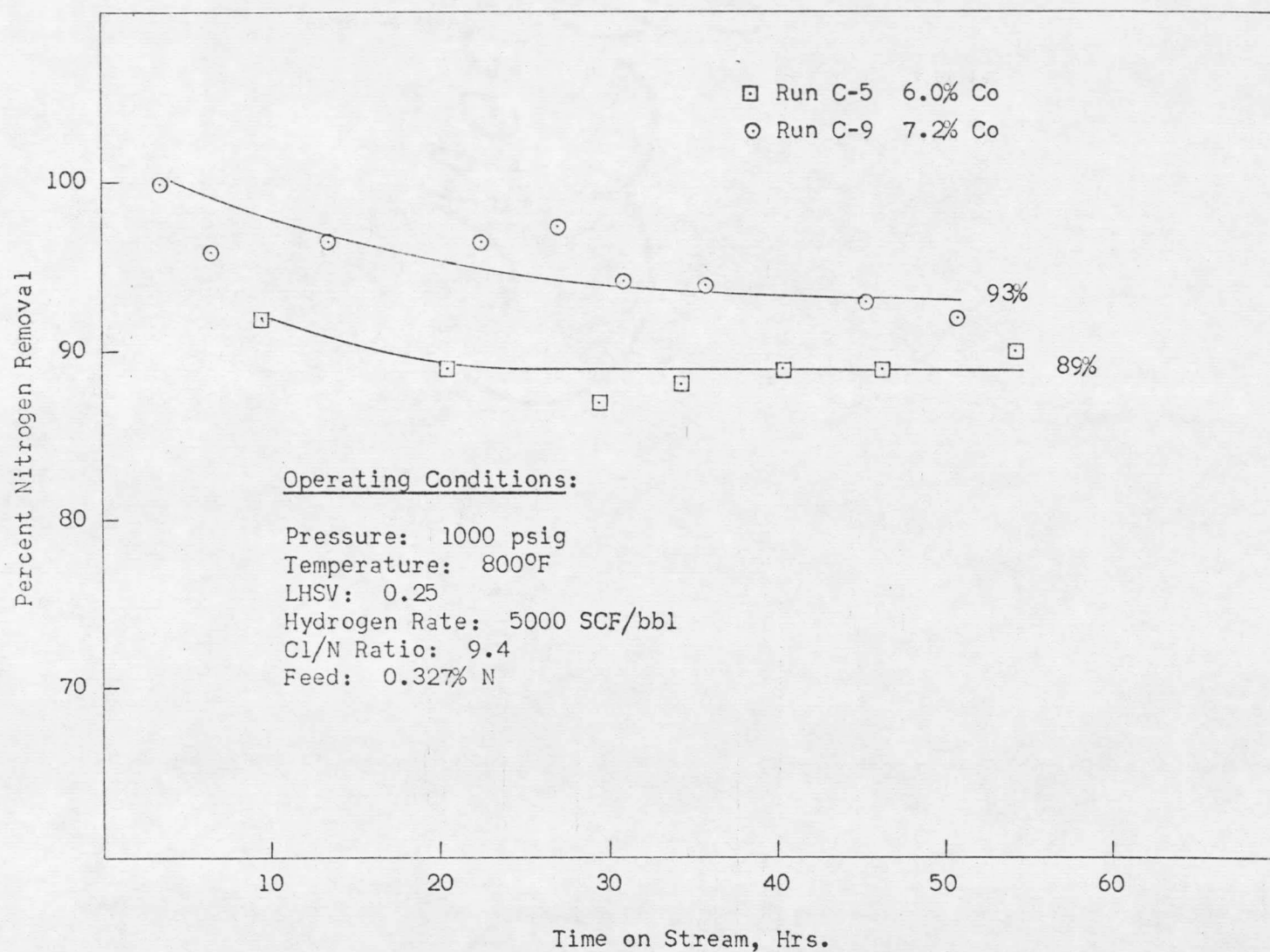


Figure 9. Preliminary Runs Using Cobaltous Chloride on Alumina-Silica Support.

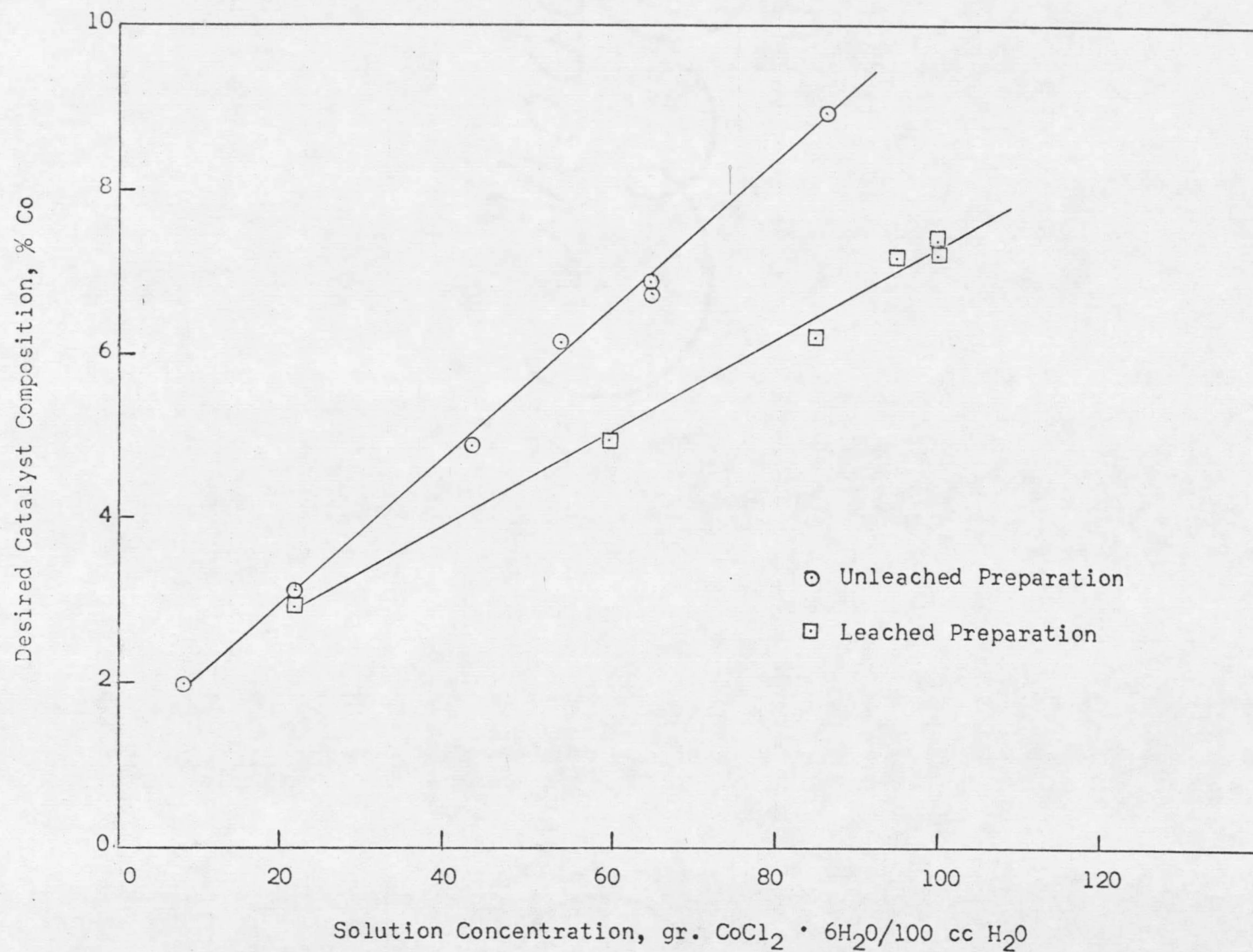


Figure 10. Solution Concentration Required for Desired Catalyst Impregnation, Harshaw 1602-T.

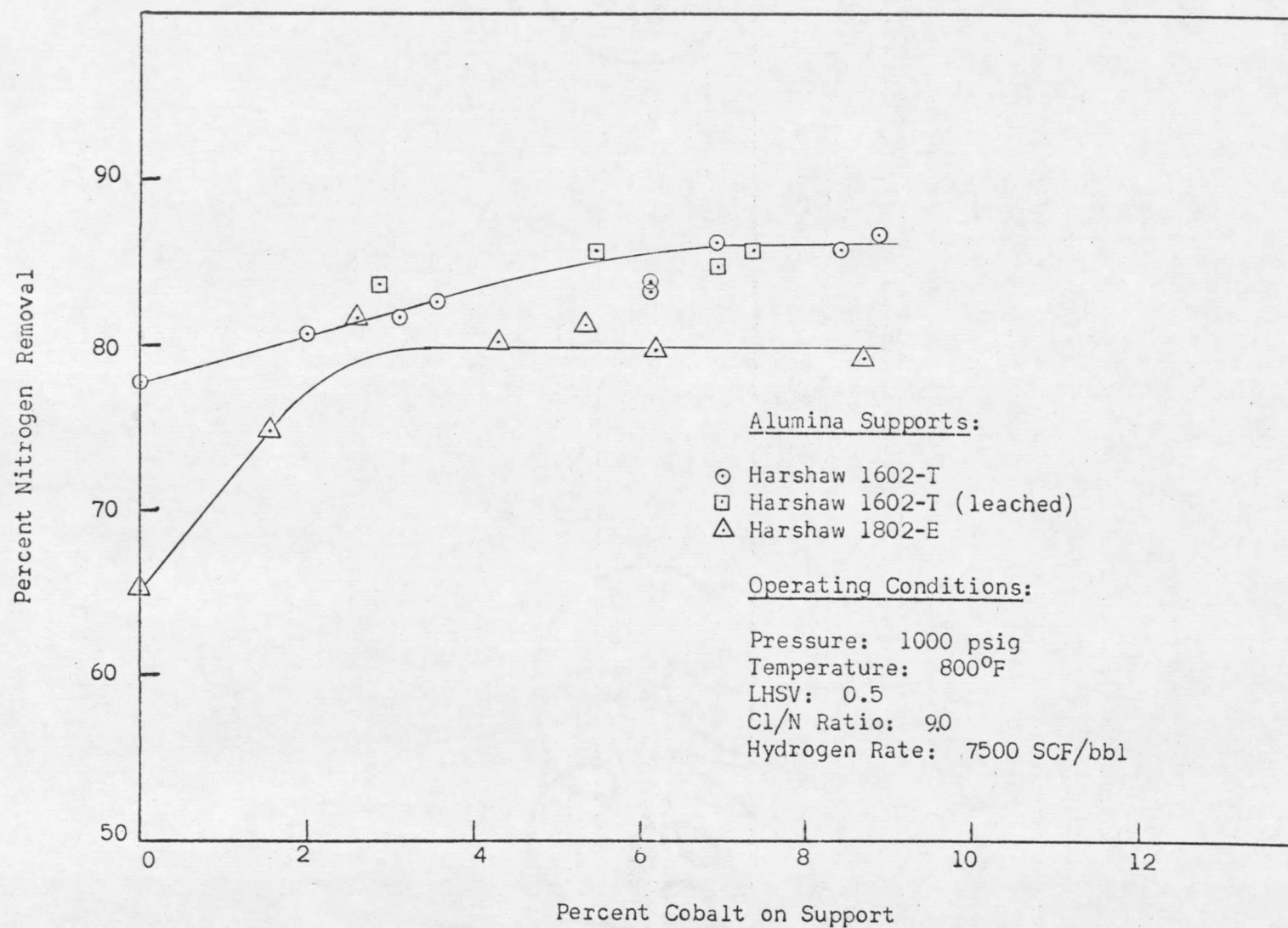


Figure 11. Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodenitrogenation Catalyst Activity.

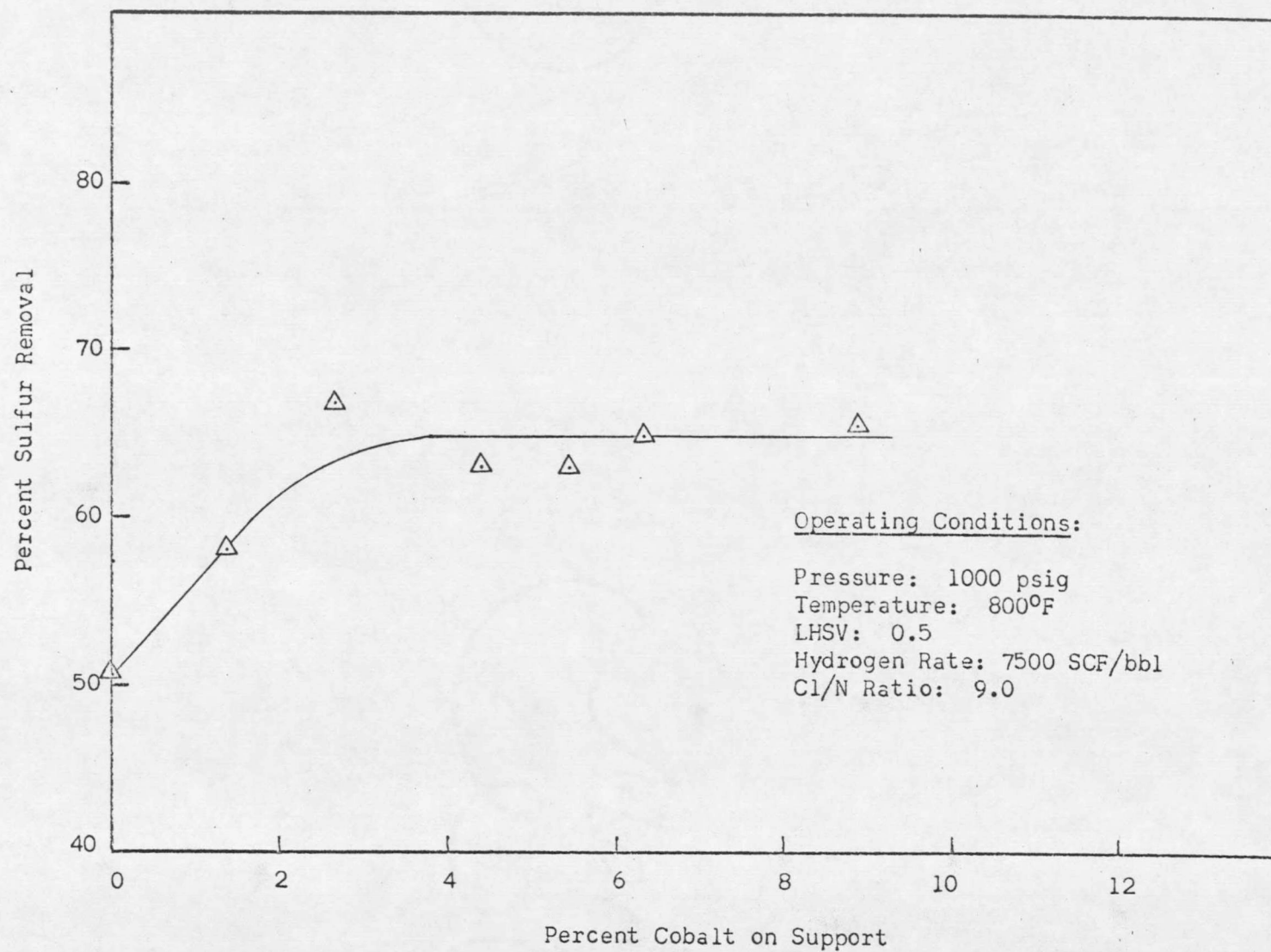


Figure 12. Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodesulfurization Activity -- Harshaw 1802-E Support.

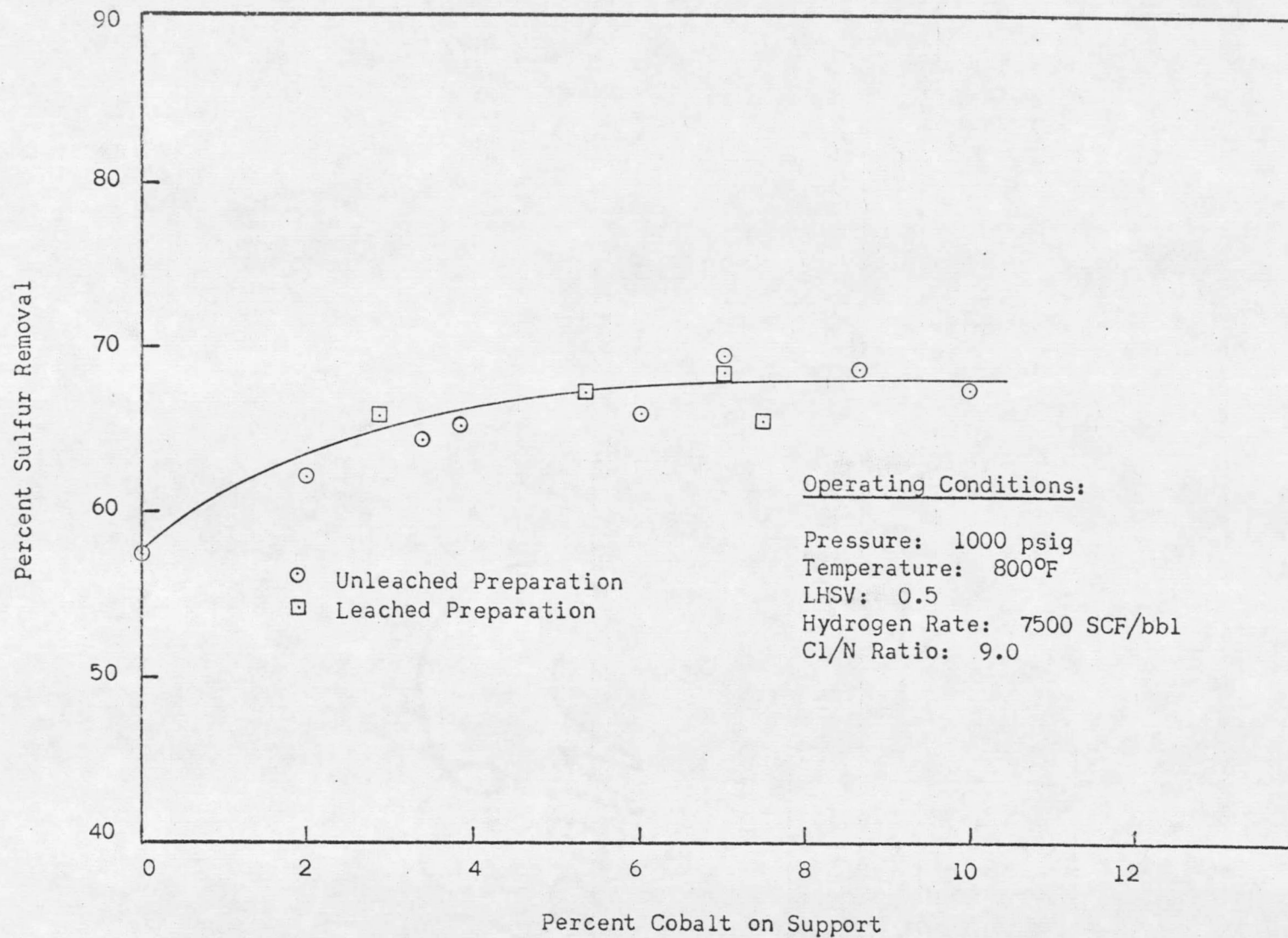


Figure 13. Effect of Percent Cobalt as Cobaltous Chloride on the Hydrodesulfurization Activity -- Harshaw 1602-T Support.

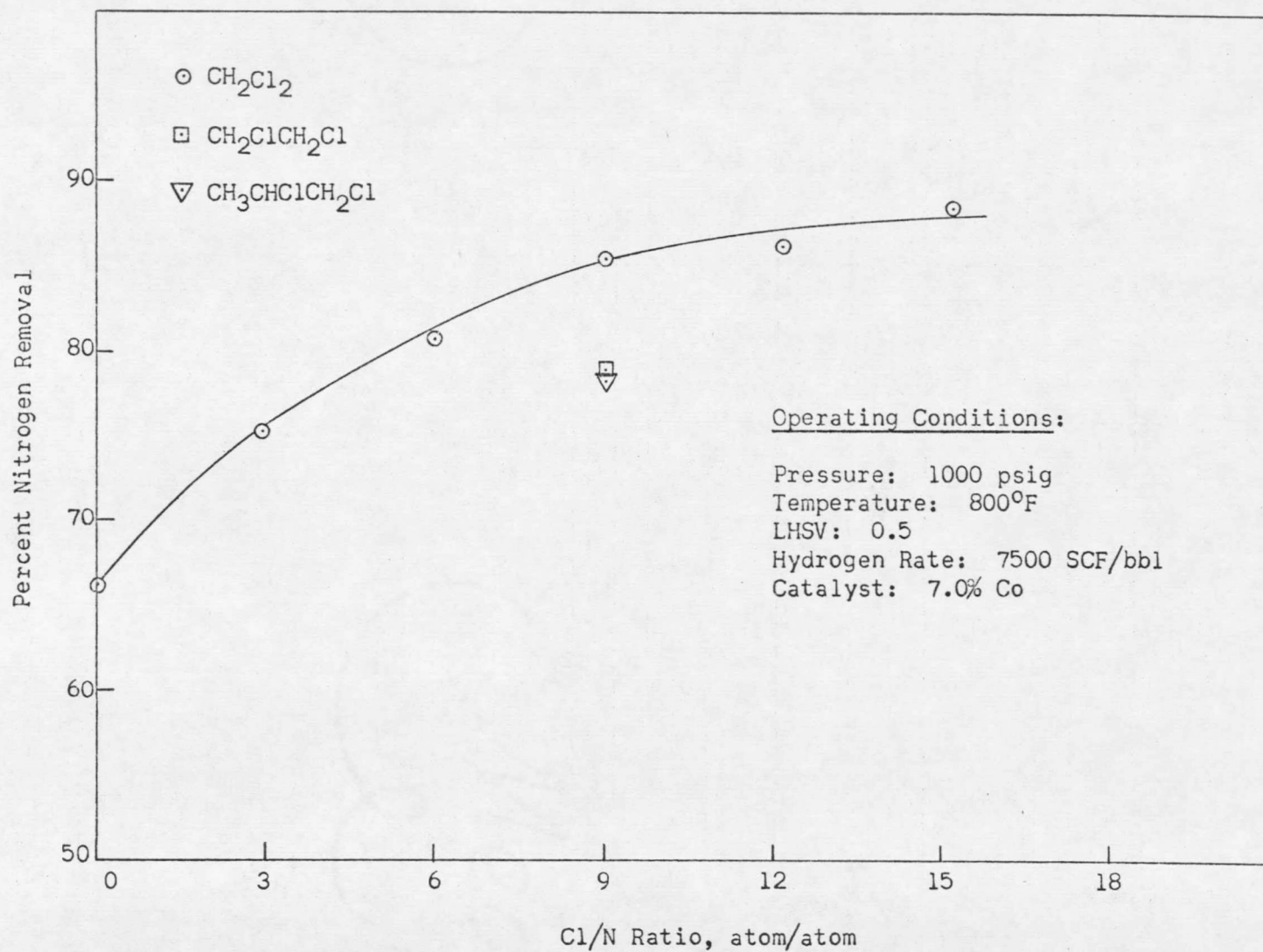


Figure 14. Effect of Chlorine-Nitrogen Ratio on the Hydrodenitrogenation Catalyst Activity.

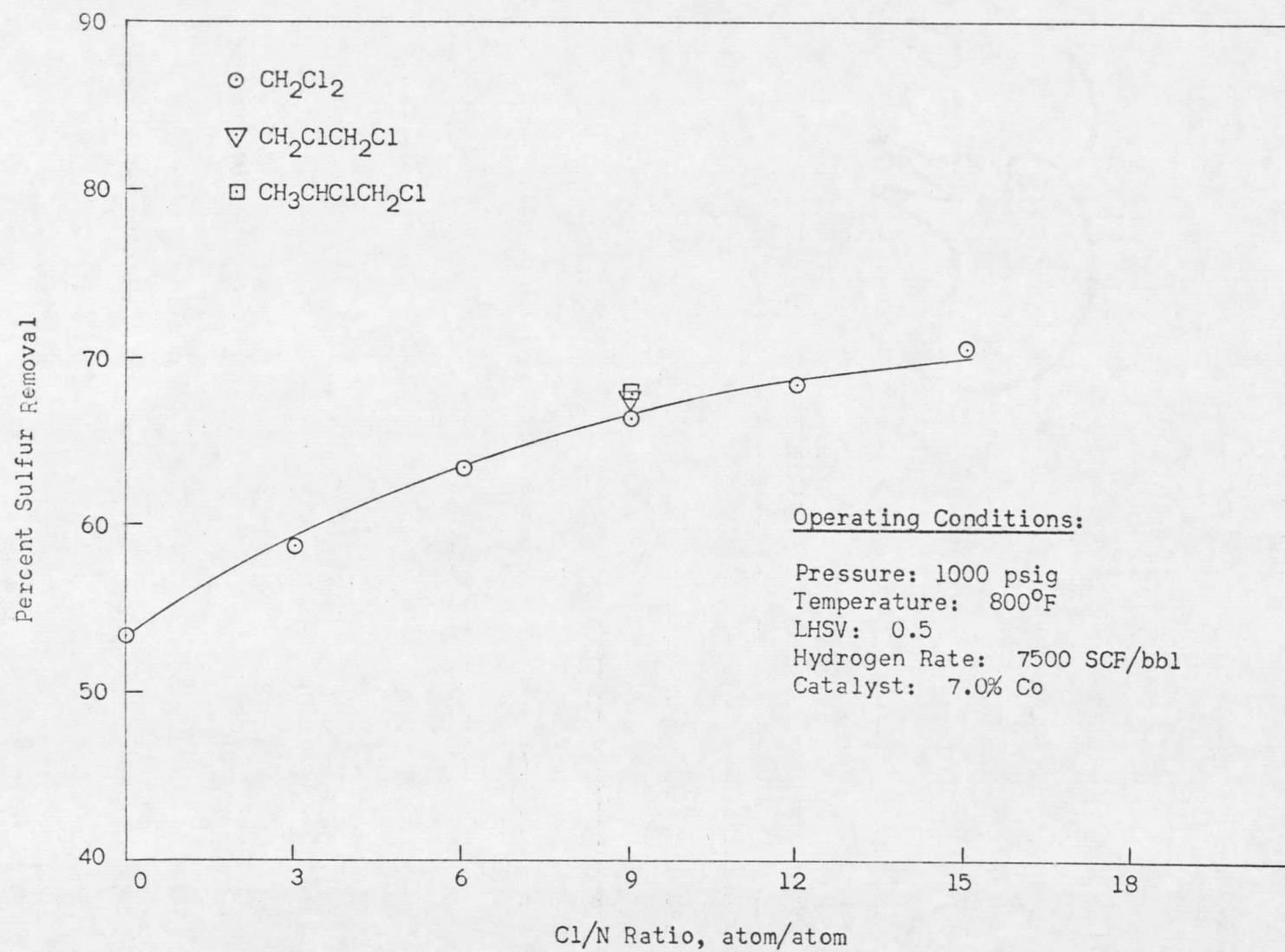


Figure 15. Effect of Chlorine-Nitrogen Ratio on the Hydrodesulfurization Activity.

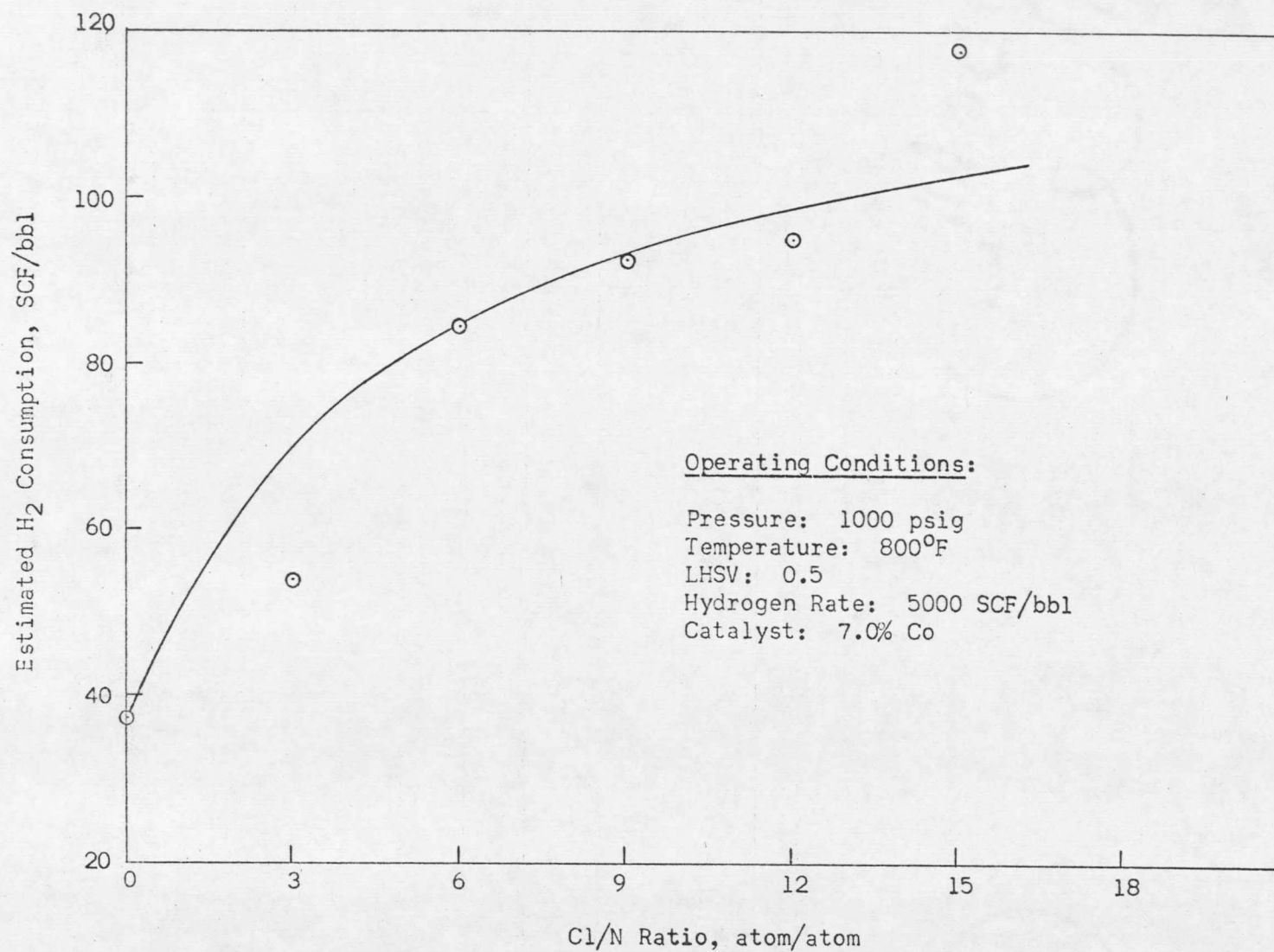


Figure 16. Effect of Chlorine-Nitrogen Ratio on Estimated Hydrogen Consumption.

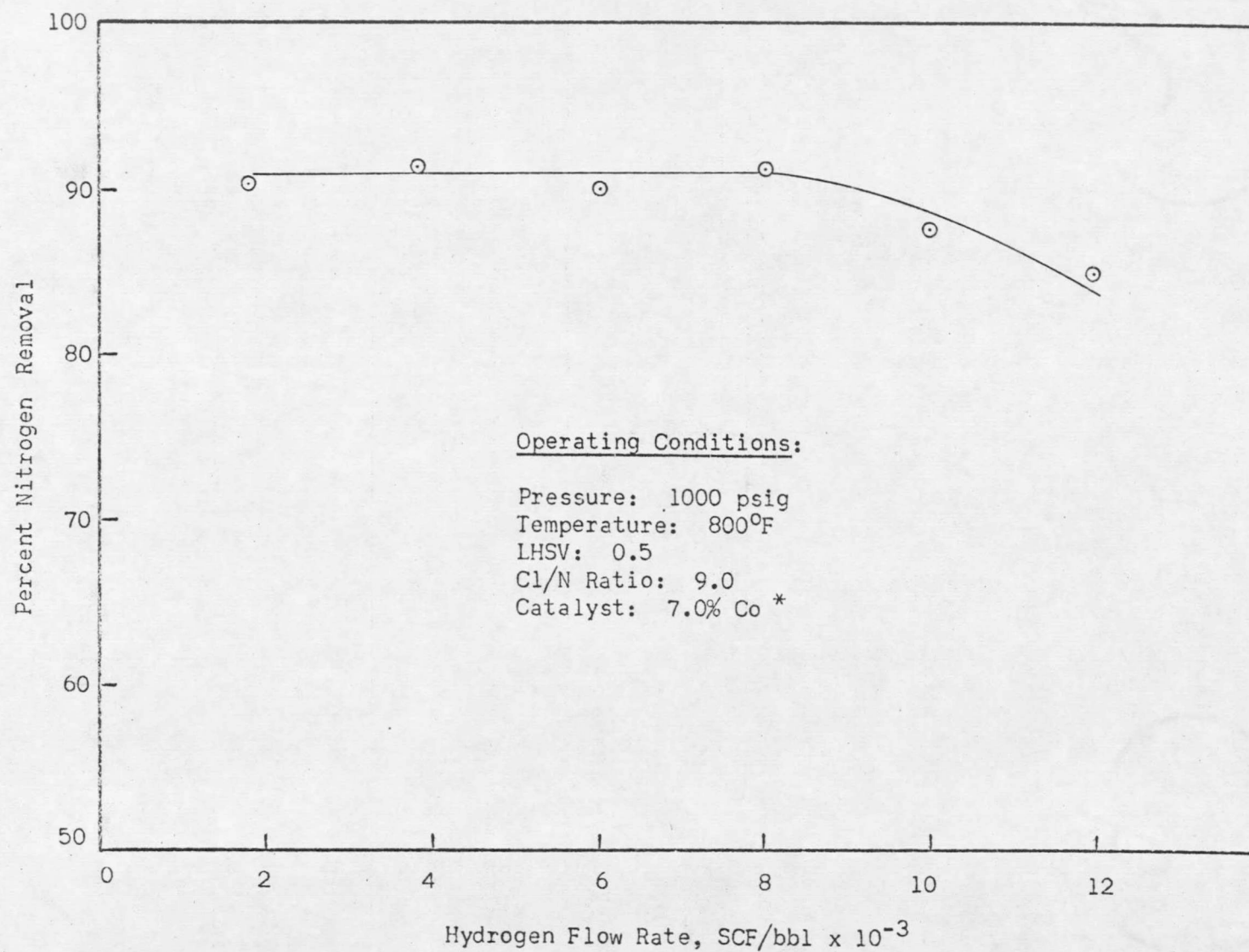


Figure 17. Effect of Hydrogen Flow Rate on the Hydrodenitrogenation Catalyst Activity.

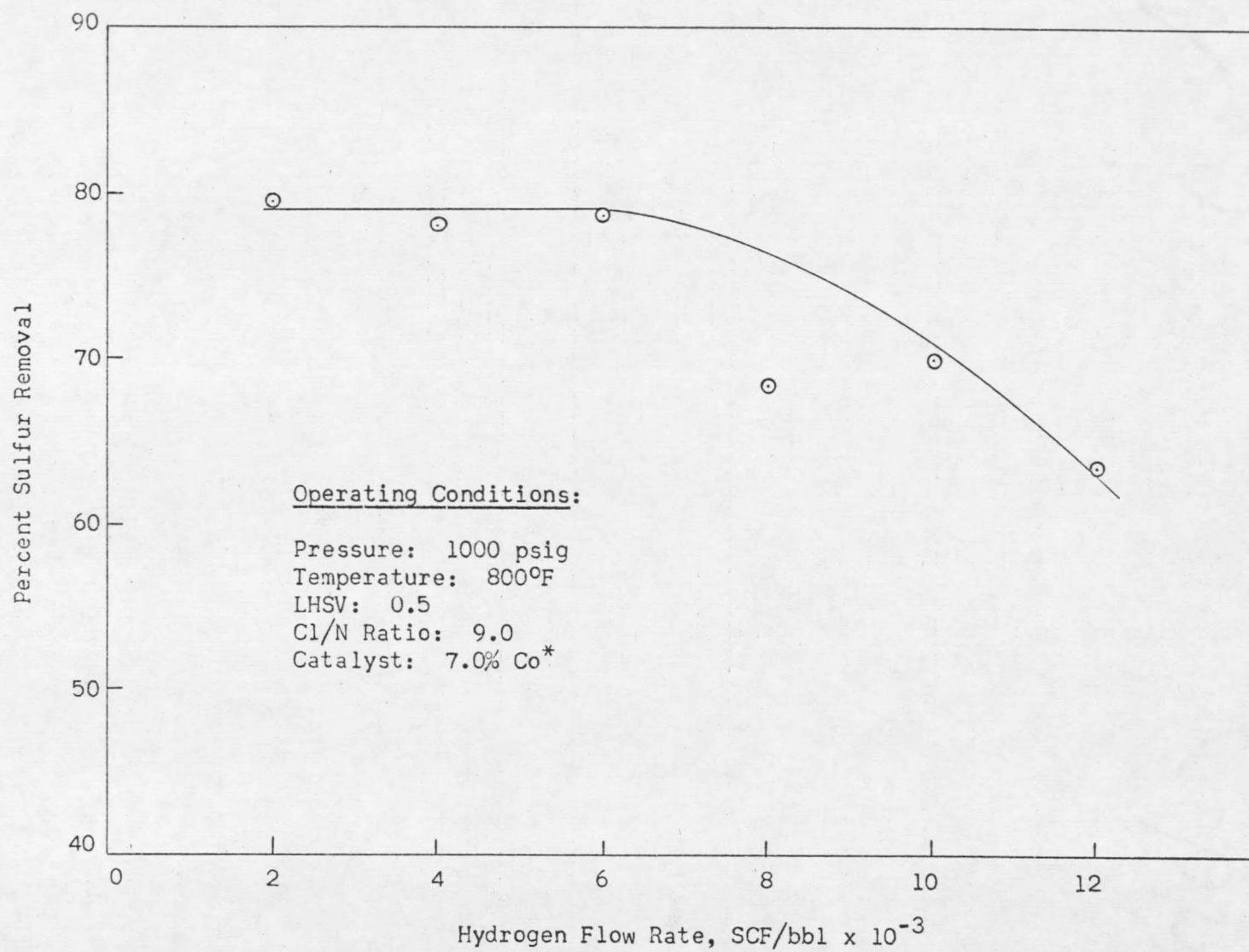


Figure 18. Effect of Hydrogen Flow Rate on the Desulfurization Activity.

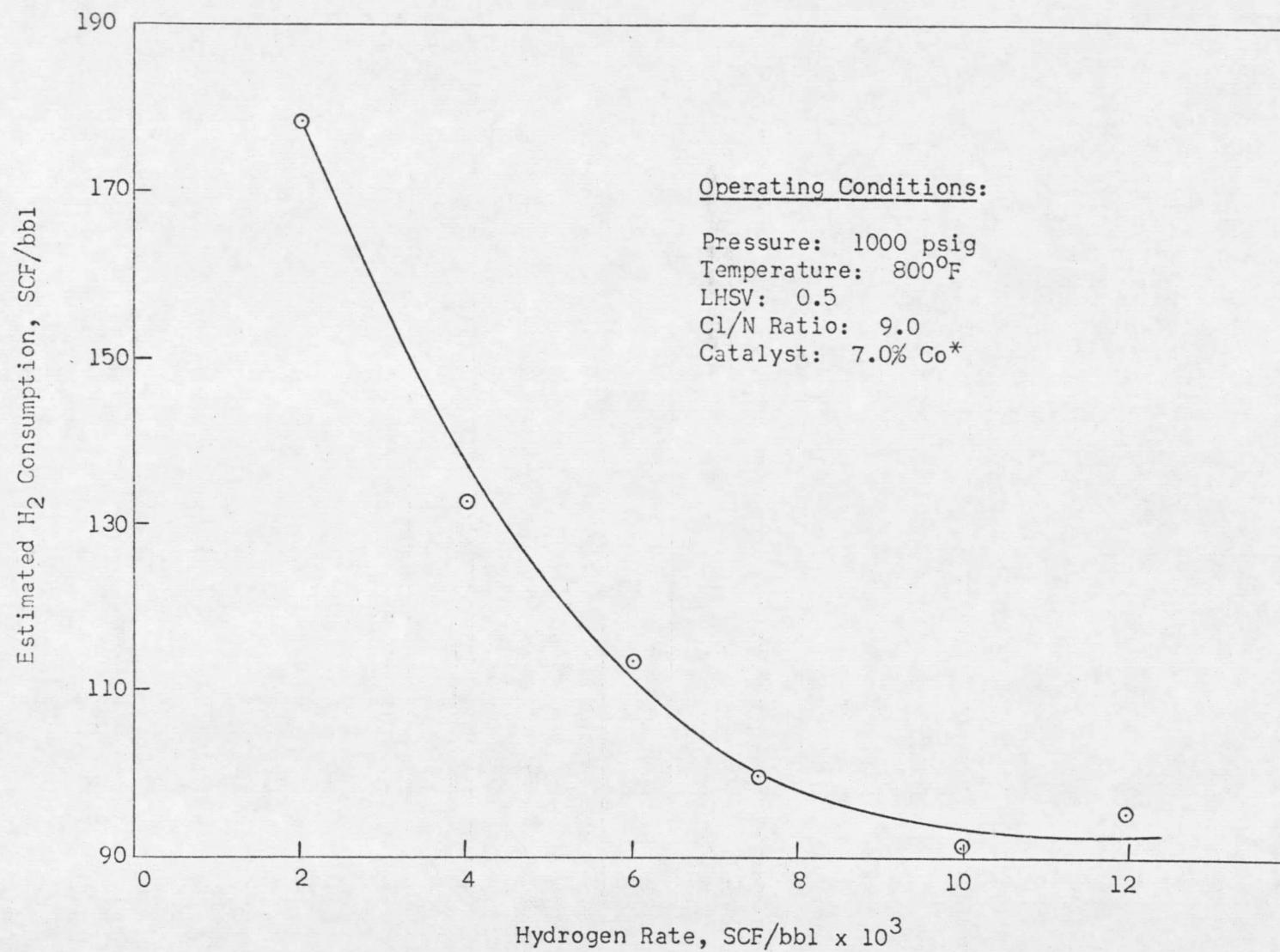


Figure 19. Effect of Hydrogen Flow Rate on Estimated Hydrogen Consumption.

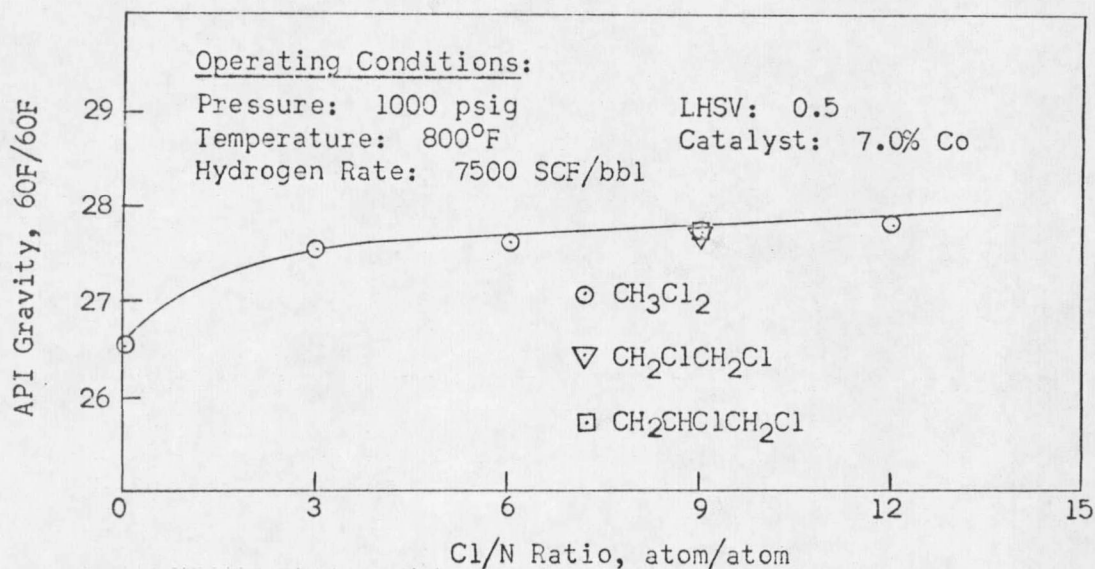


Figure 20. Effect of Chlorine-Nitrogen Ratio on Product Gravity.

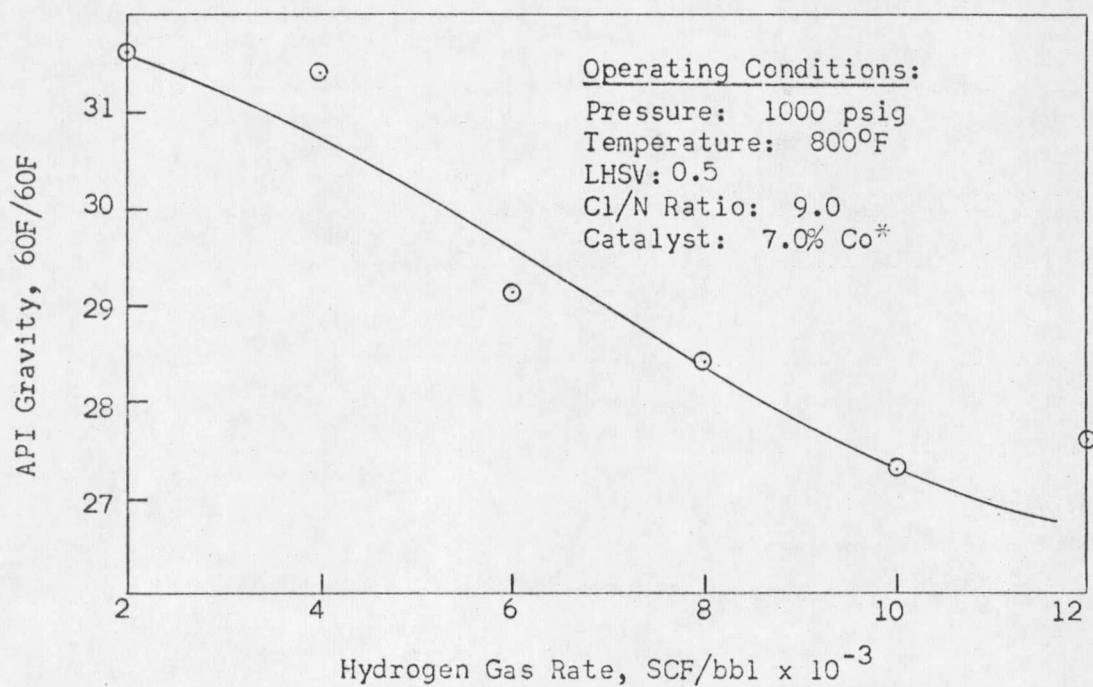


Figure 21. Effect of Hydrogen Flow Rate on Product Gravity.

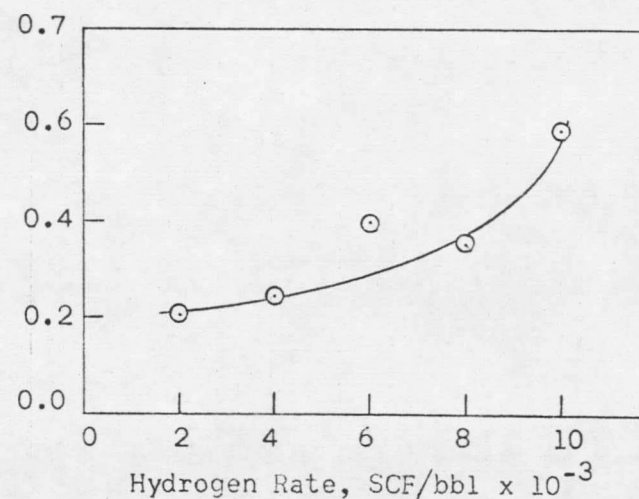
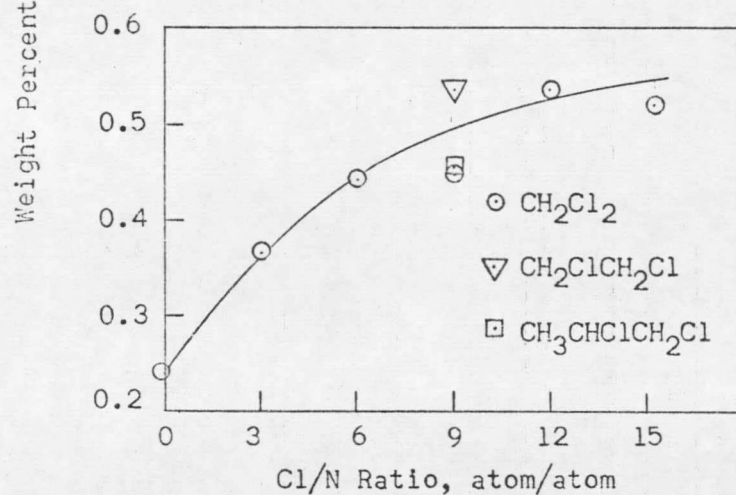
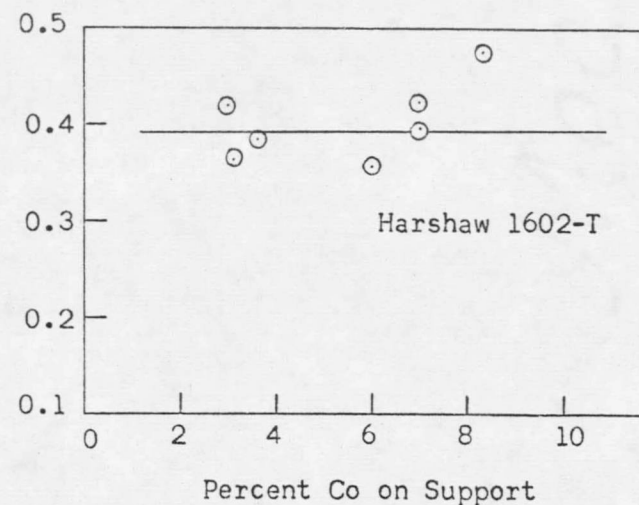
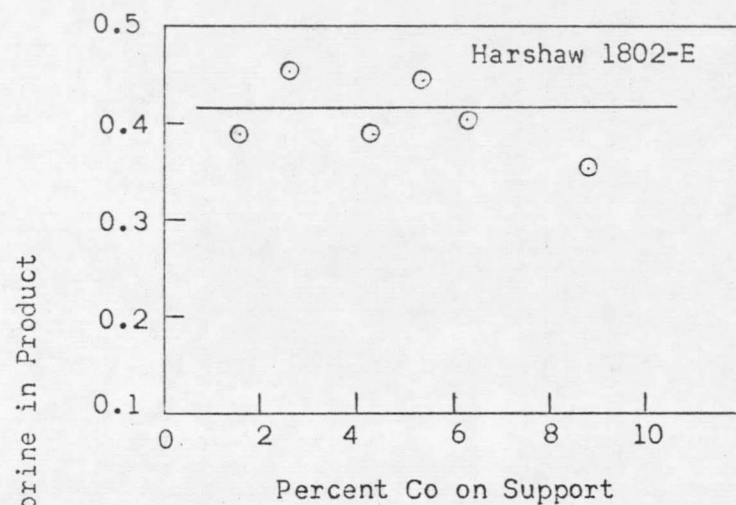


Figure 22. Effect of Percent Cobalt on Support, Chlorine-Nitrogen Ratio and Hydrogen Flow Rate on Weight Percent Chlorine in Product.

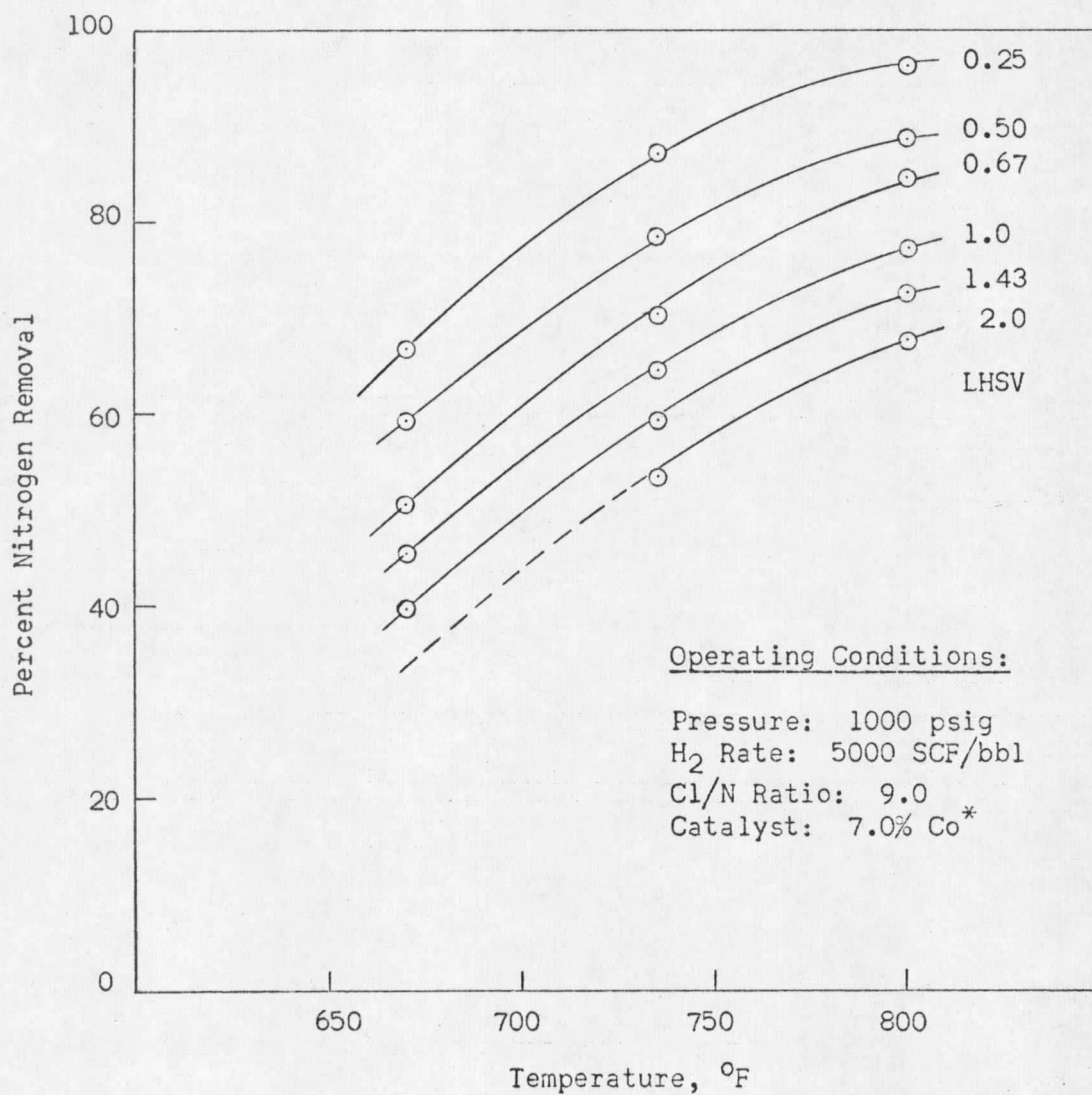


Figure 23. Effect of Temperature and Space Velocity on the Hydrodenitrogenation Catalyst Activity.

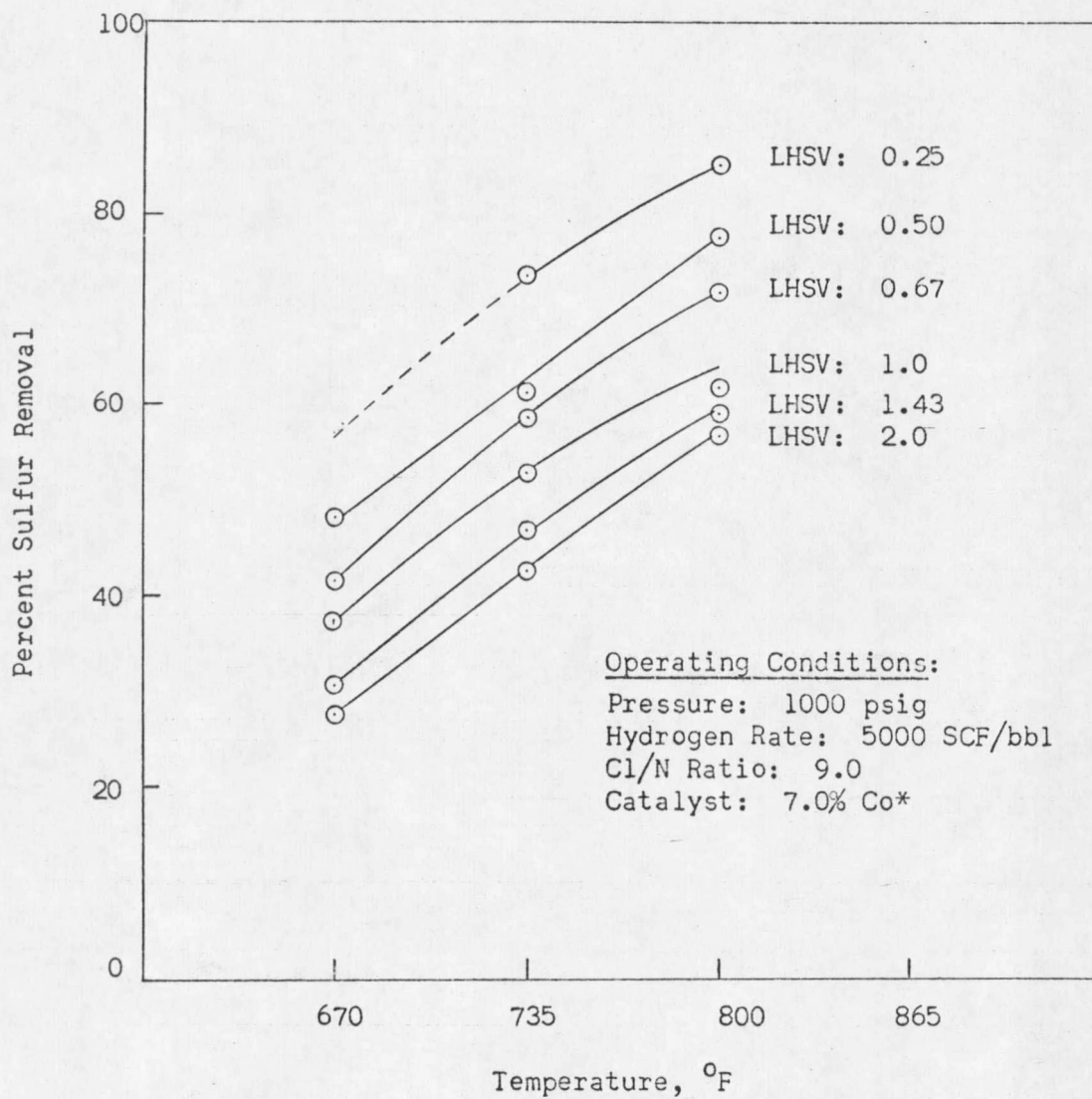


Figure 24. Effect of Temperature and Space Velocity on the Hydrodesulfurization Activity.

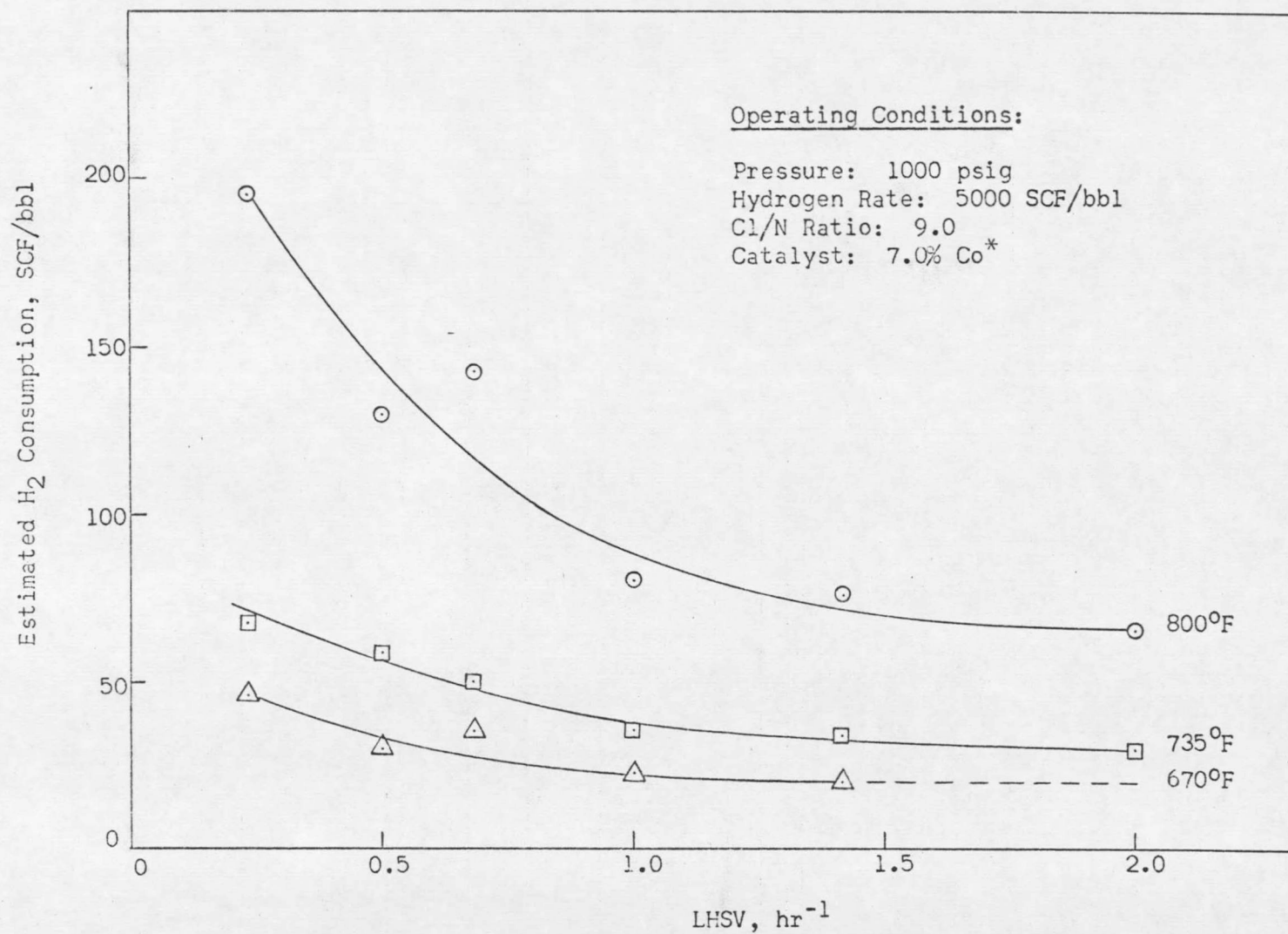


Figure 25. Effect of Space Velocity and Temperature on Estimated Hydrogen Consumption.

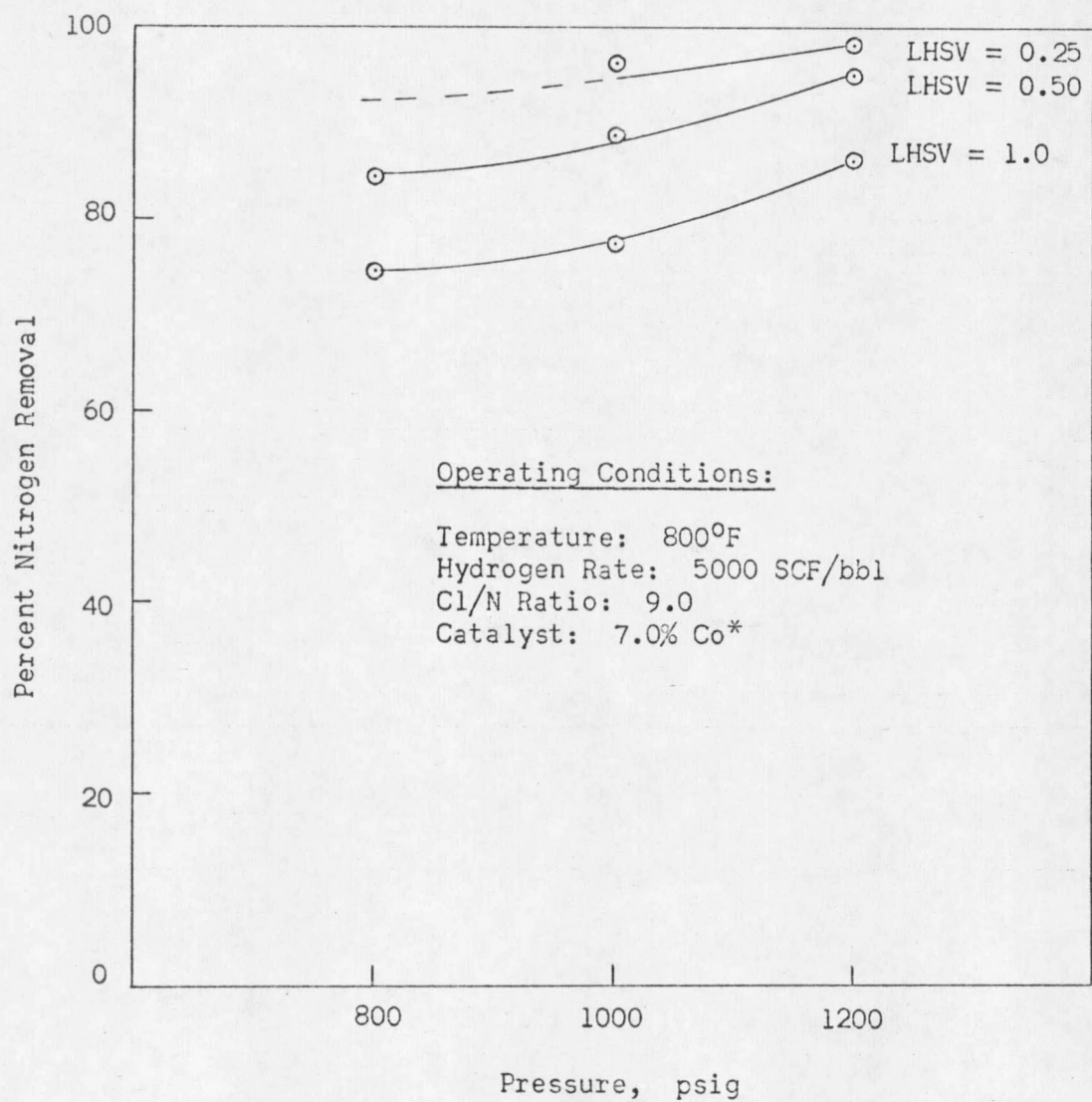


Figure 26. Effect of Pressure and Space Velocity on the Hydrodenitrogenation Catalyst Activity.

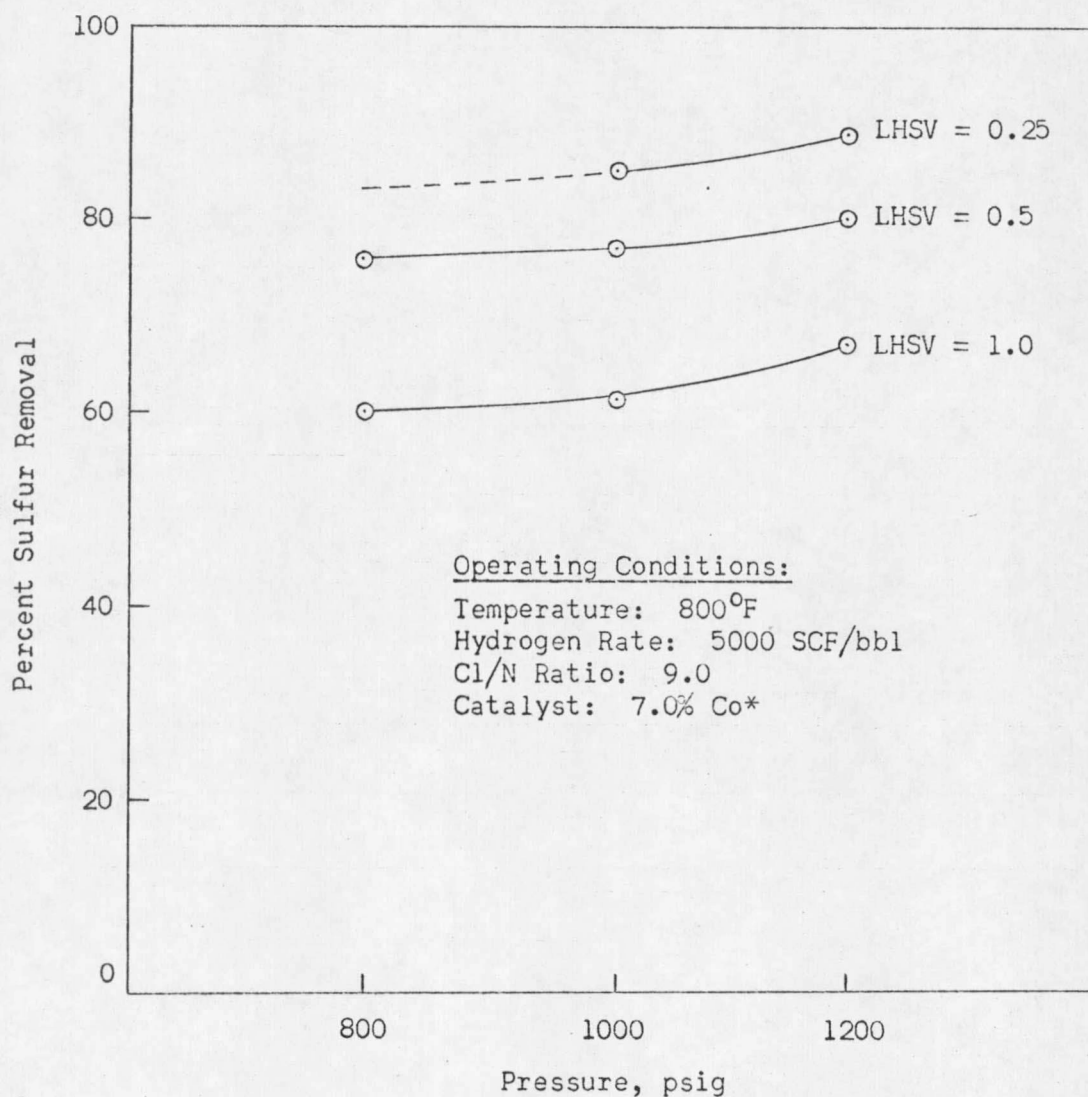


Figure 27. Effect of Pressure and Space Velocity on Hydrodesulfurization Activity.

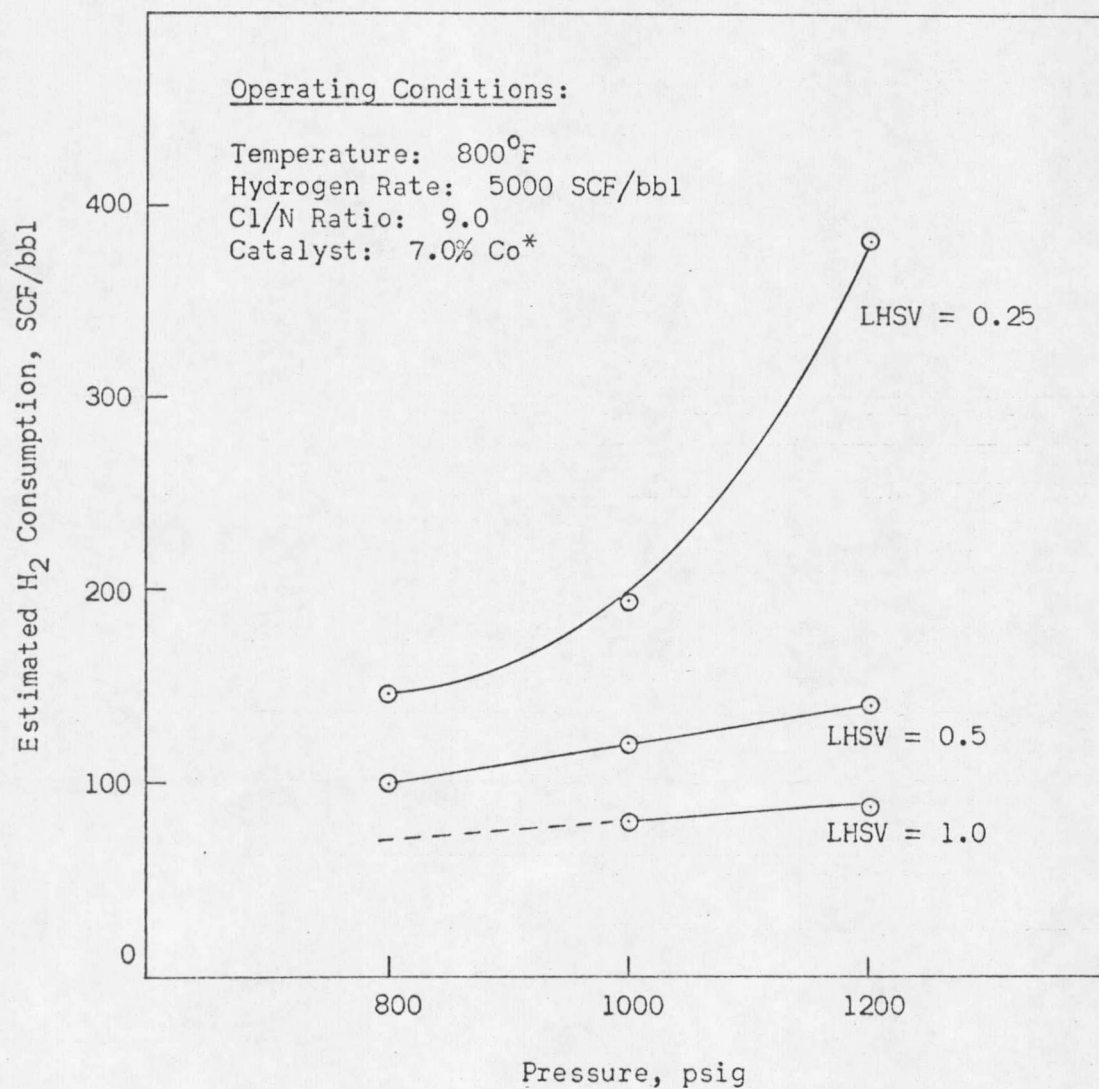


Figure 28. Effect of Pressure and Space Velocity on Estimated Hydrogen Consumption.

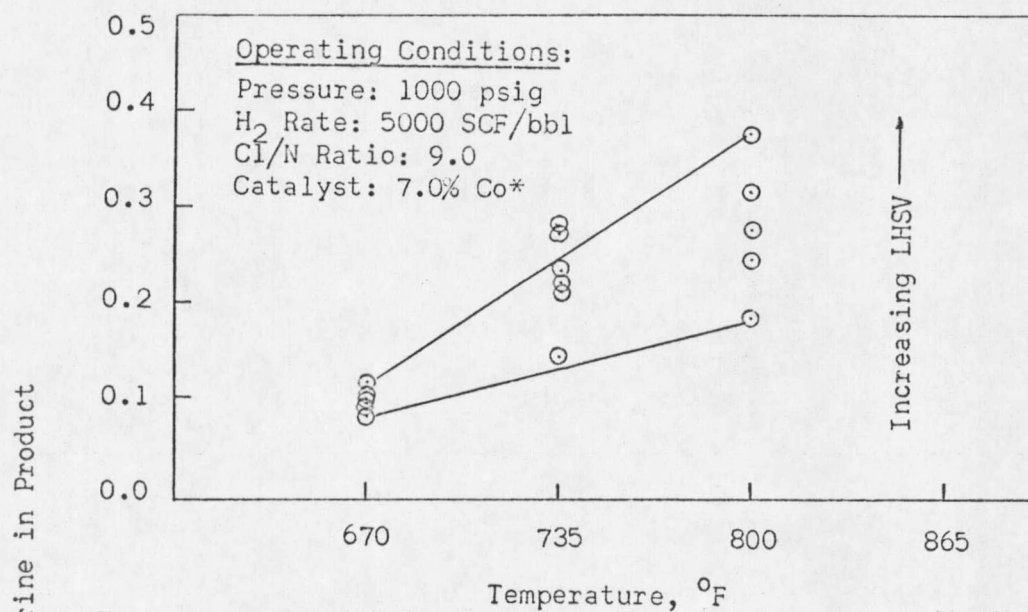


Figure 29. Effect of Temperature and Space Velocity on Weight Percent Chlorine in Product.

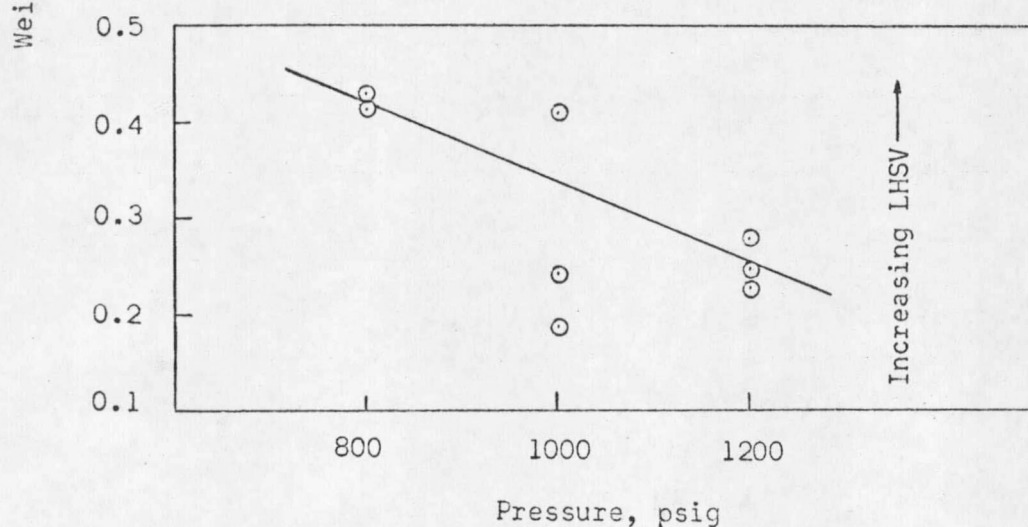


Figure 30. Effect of Pressure and Space Velocity on Weight Percent Chlorine in Product.

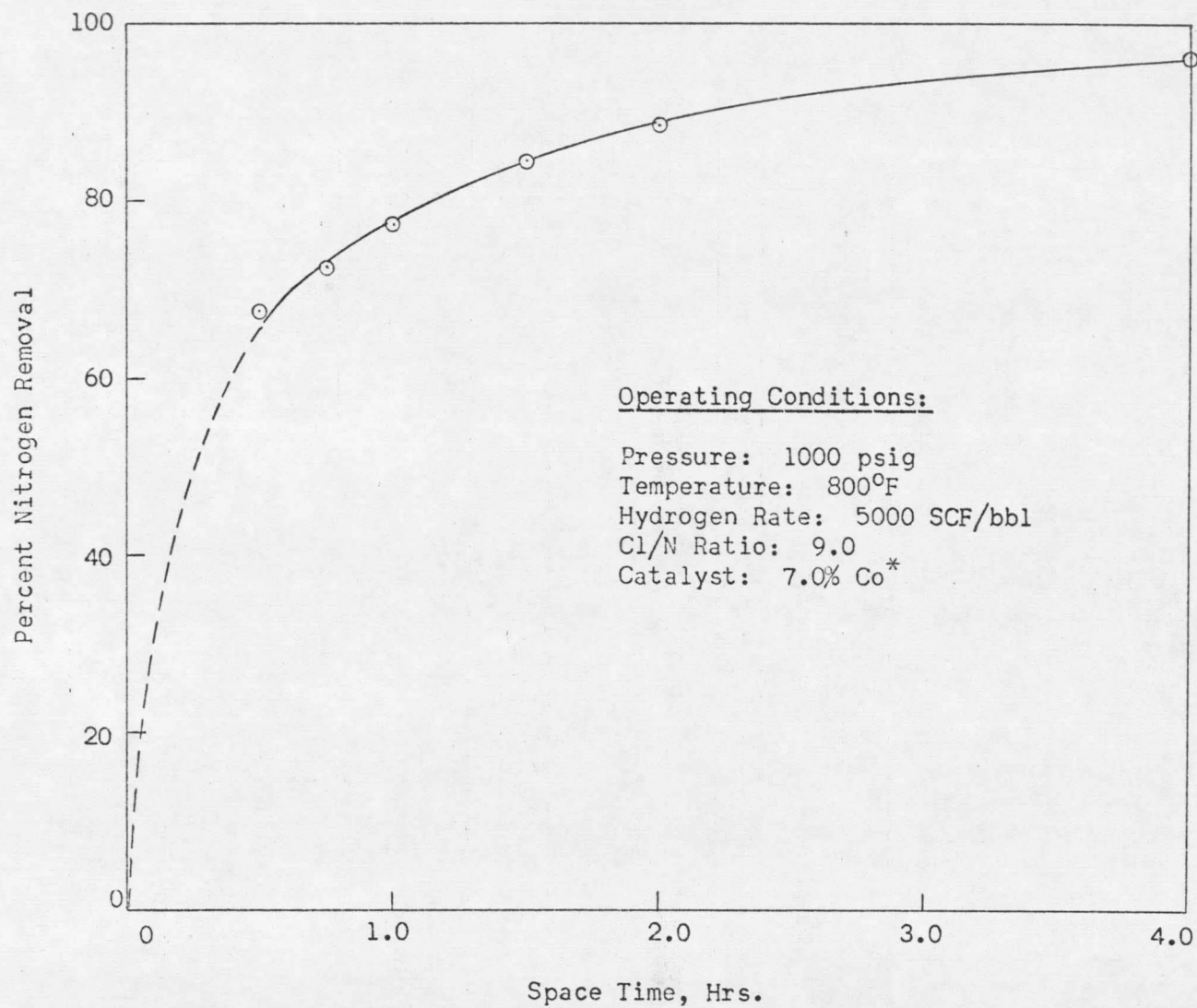


Figure 31. Effect of Space Time on the Hydrodenitrogenation Catalyst Activity, 800°F.

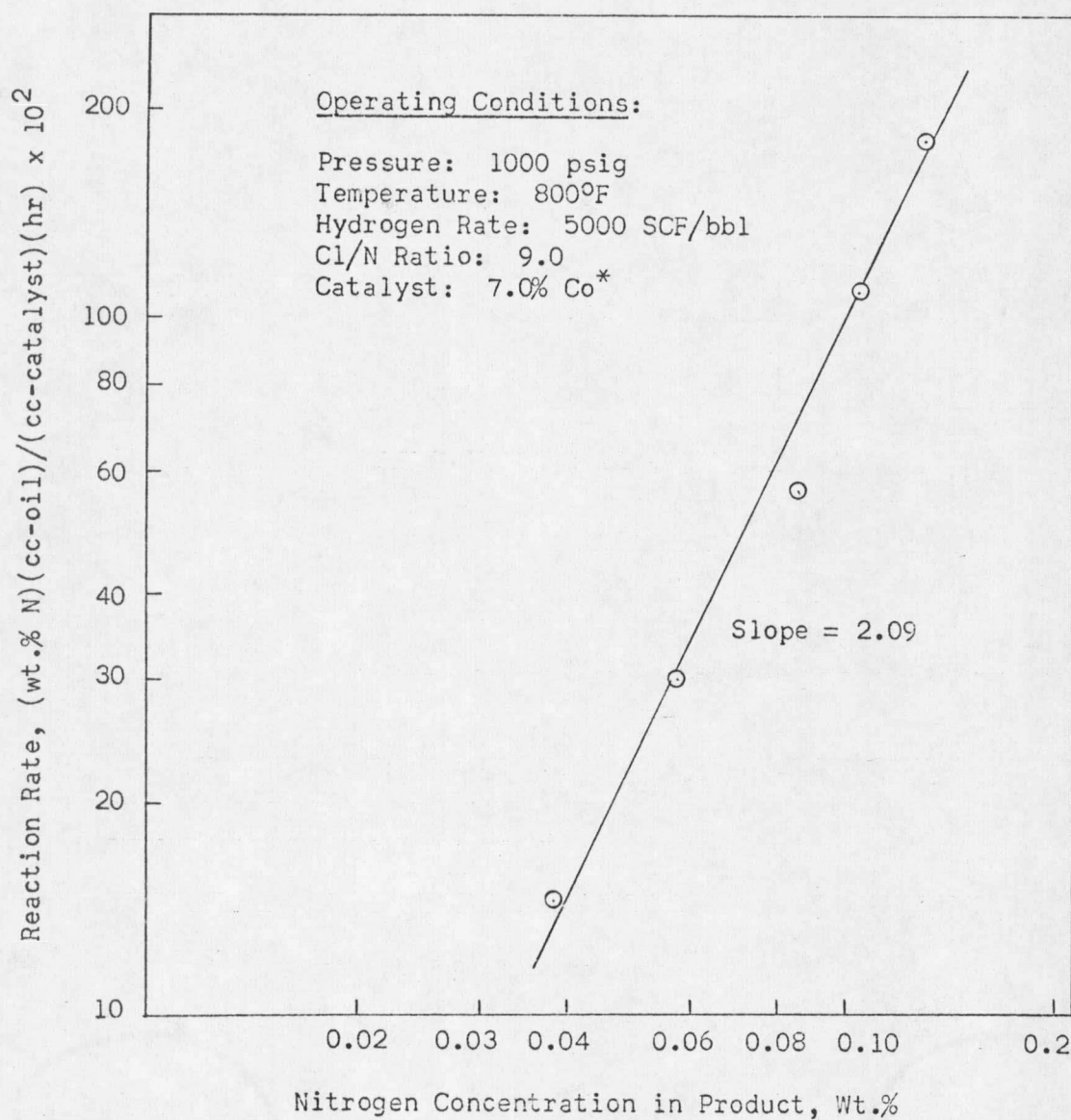


Figure 32. Pseudo Order of Reaction for Hydrodenitrogenation by Differential Analysis.

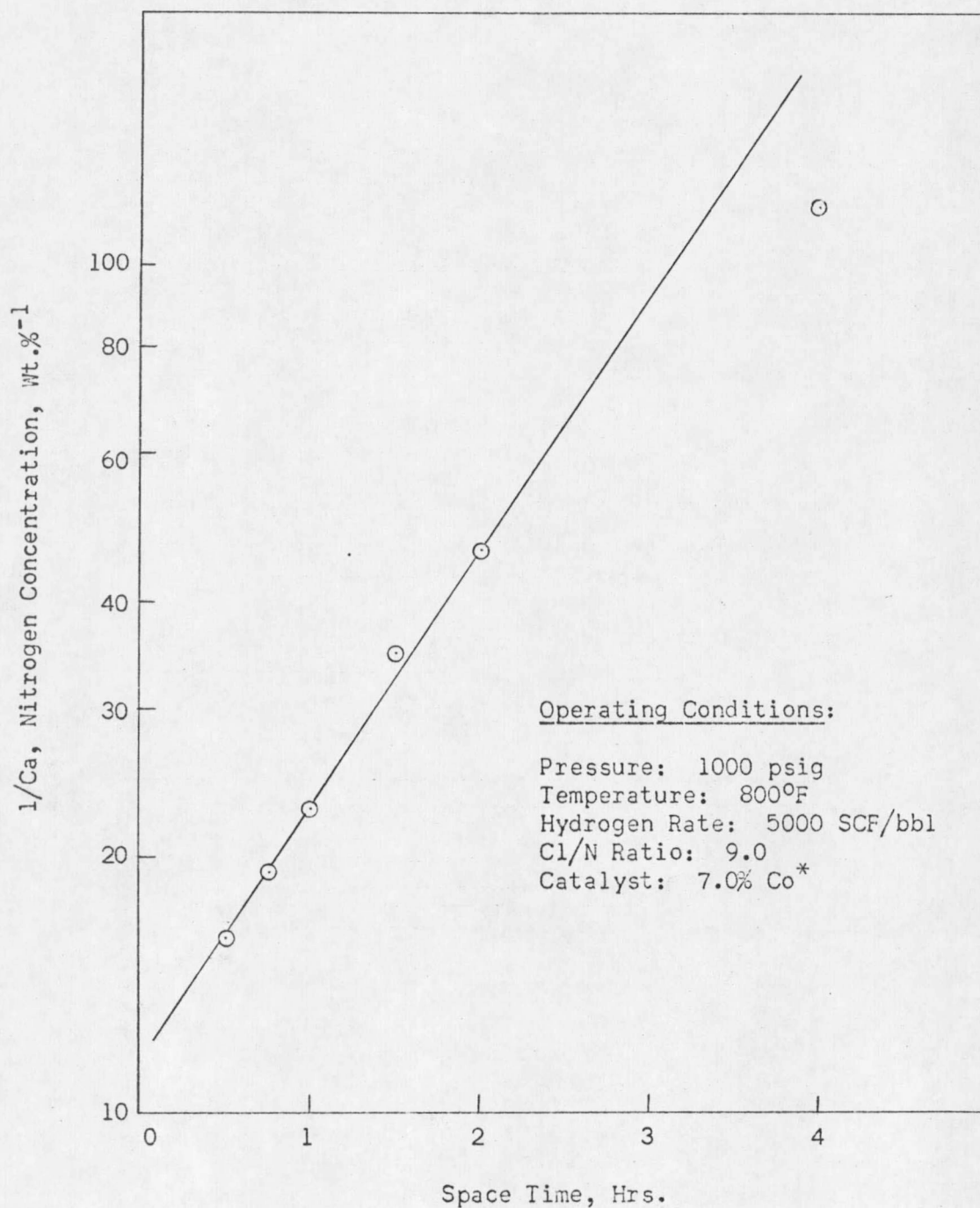


Figure 33. Test for Pseudo-Second Order Reaction for Hydrodenitrogenation.

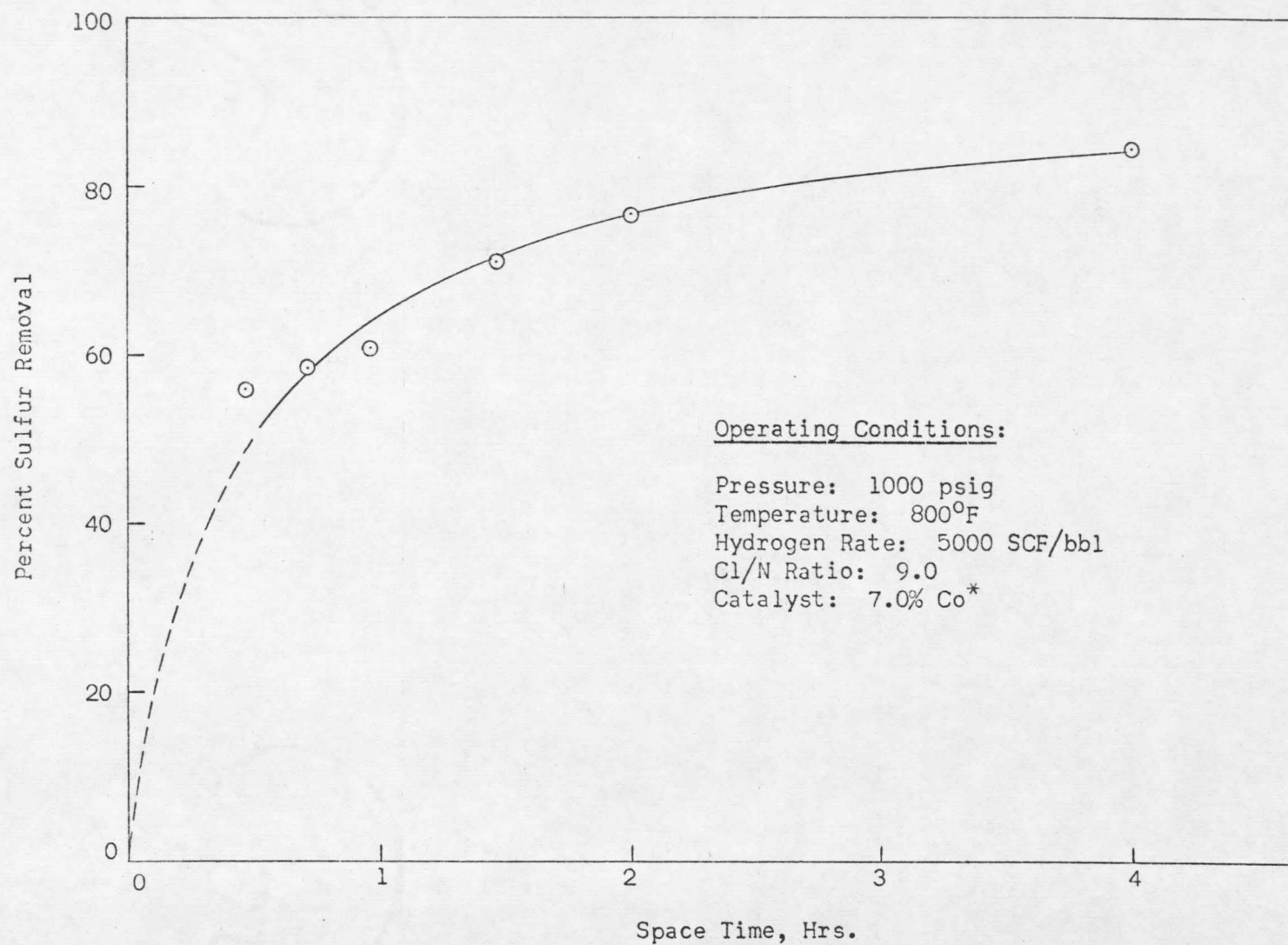


Figure 34. Effect of Space Time on the Hydrodesulfurization Activity, 800°F.

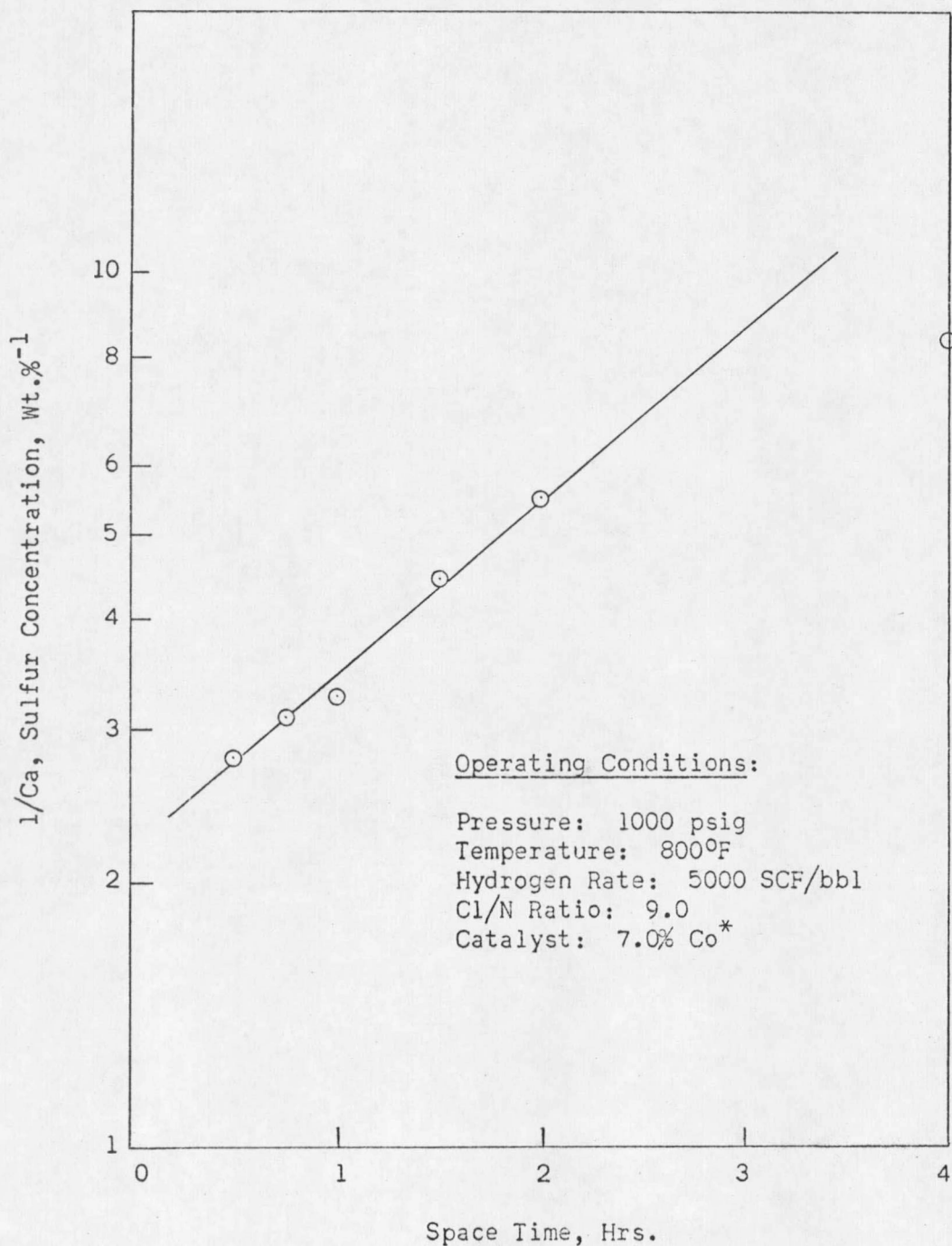


Figure 35. Test for Pseudo-Second Order Reaction for Hydrodesulfurization.

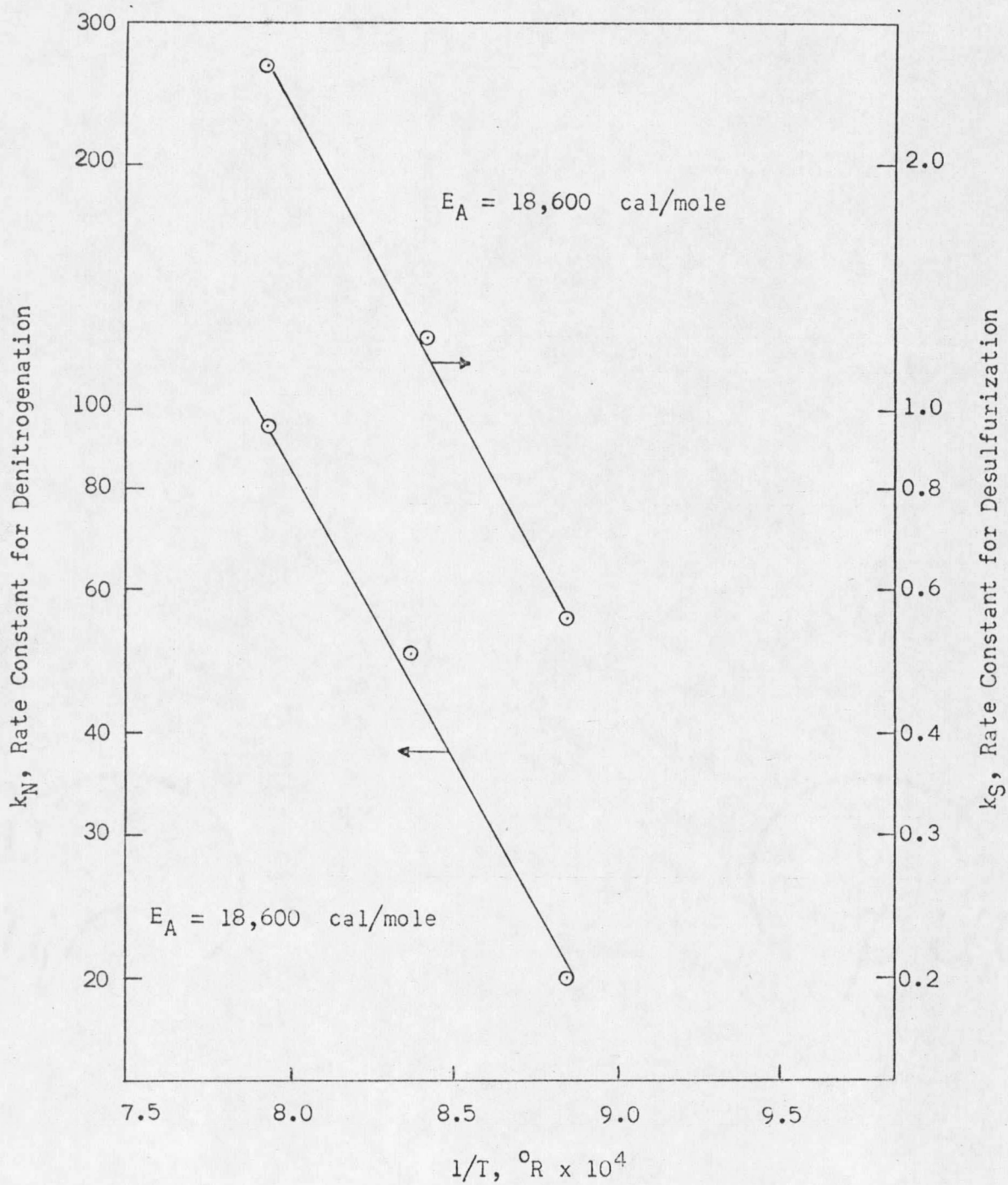
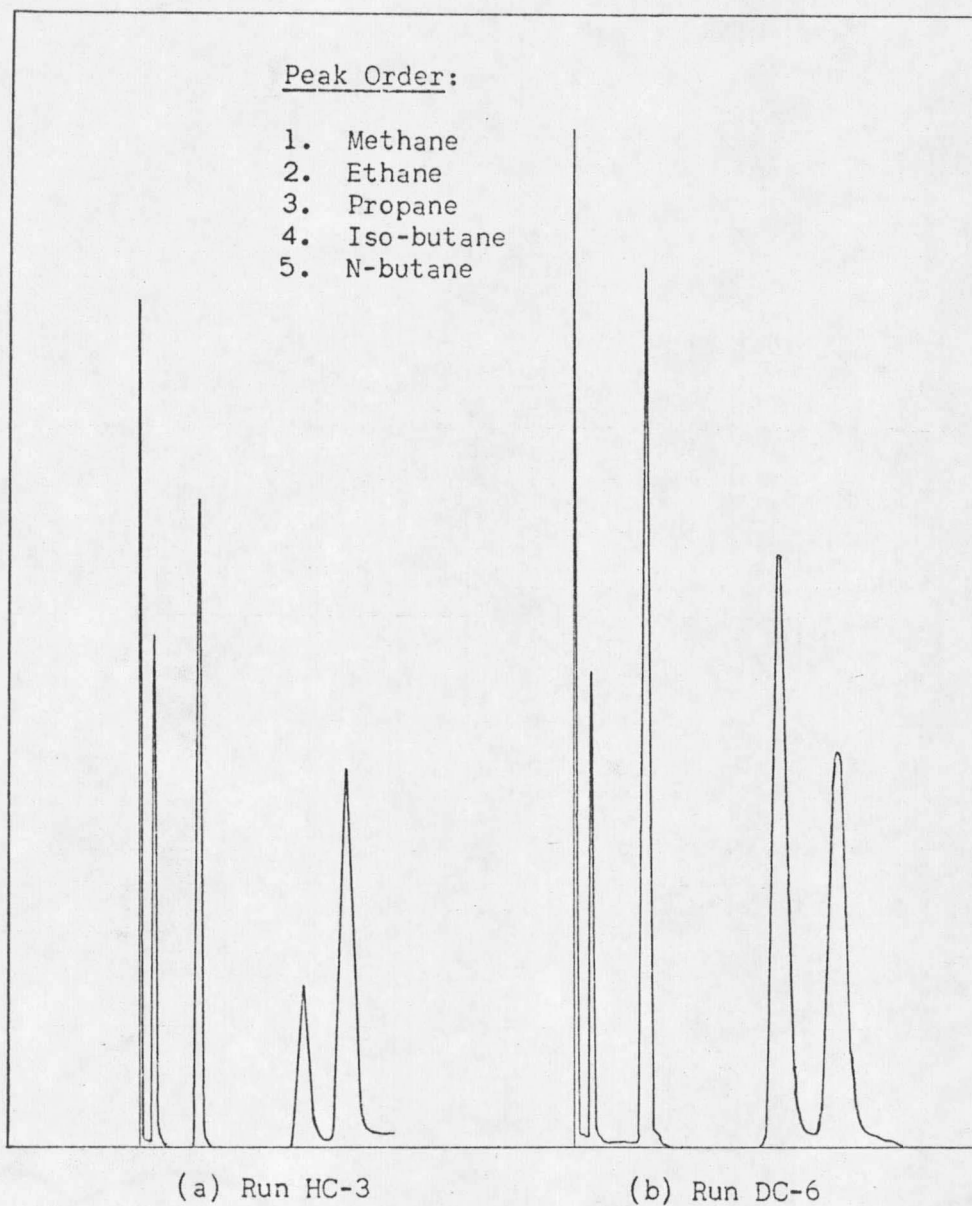


Figure 36. Activation Energy.



Attenuation and Sample Size for both traces are identical.
Hydrogen is not detected by FID.

Figure 37. Typical Gas Chromatograph Analysis Traces of
Effluent Gas from Reactor.

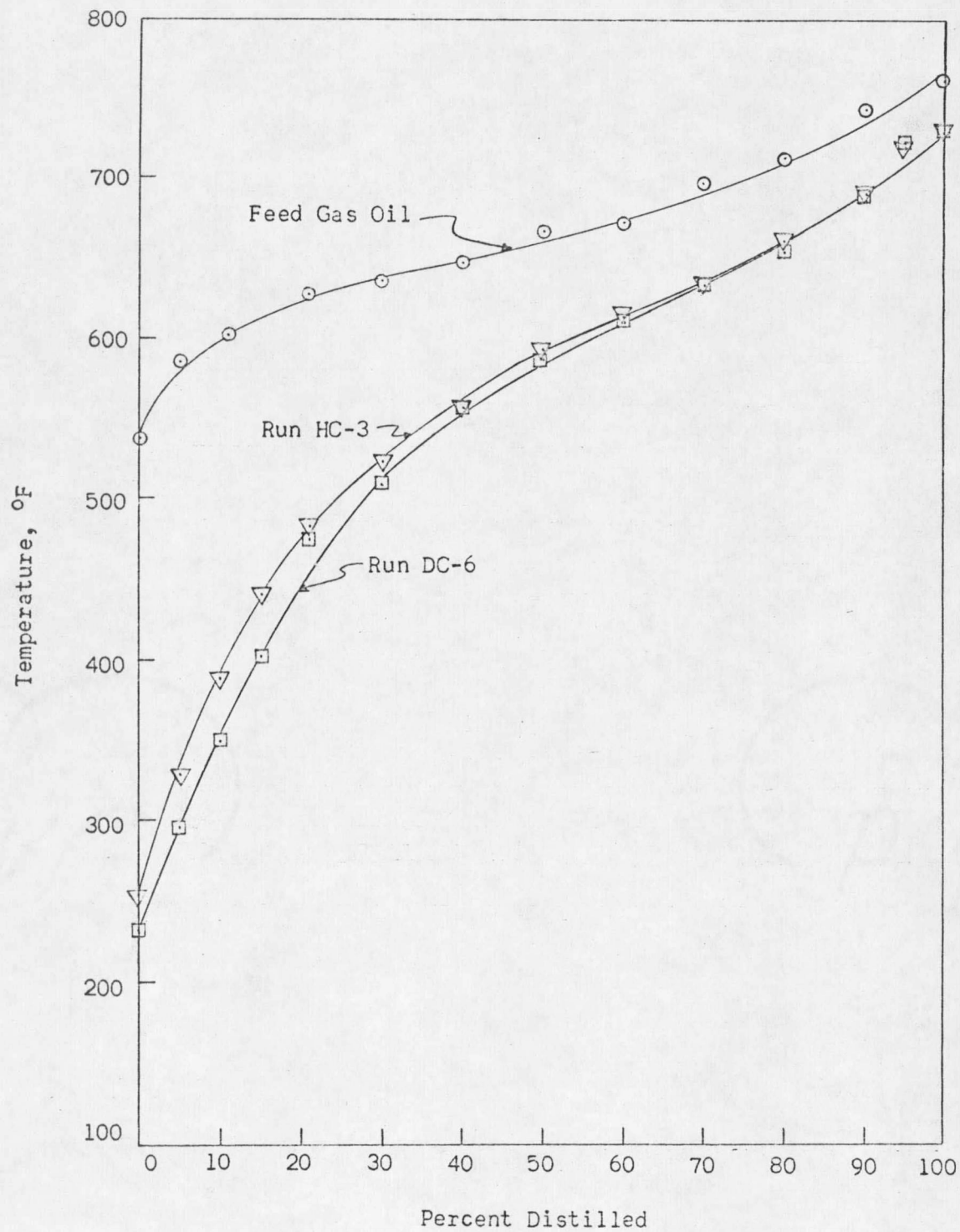


Figure 38. ASTM D-158 Distillation for the Feed and Typical Products, 760 mm.

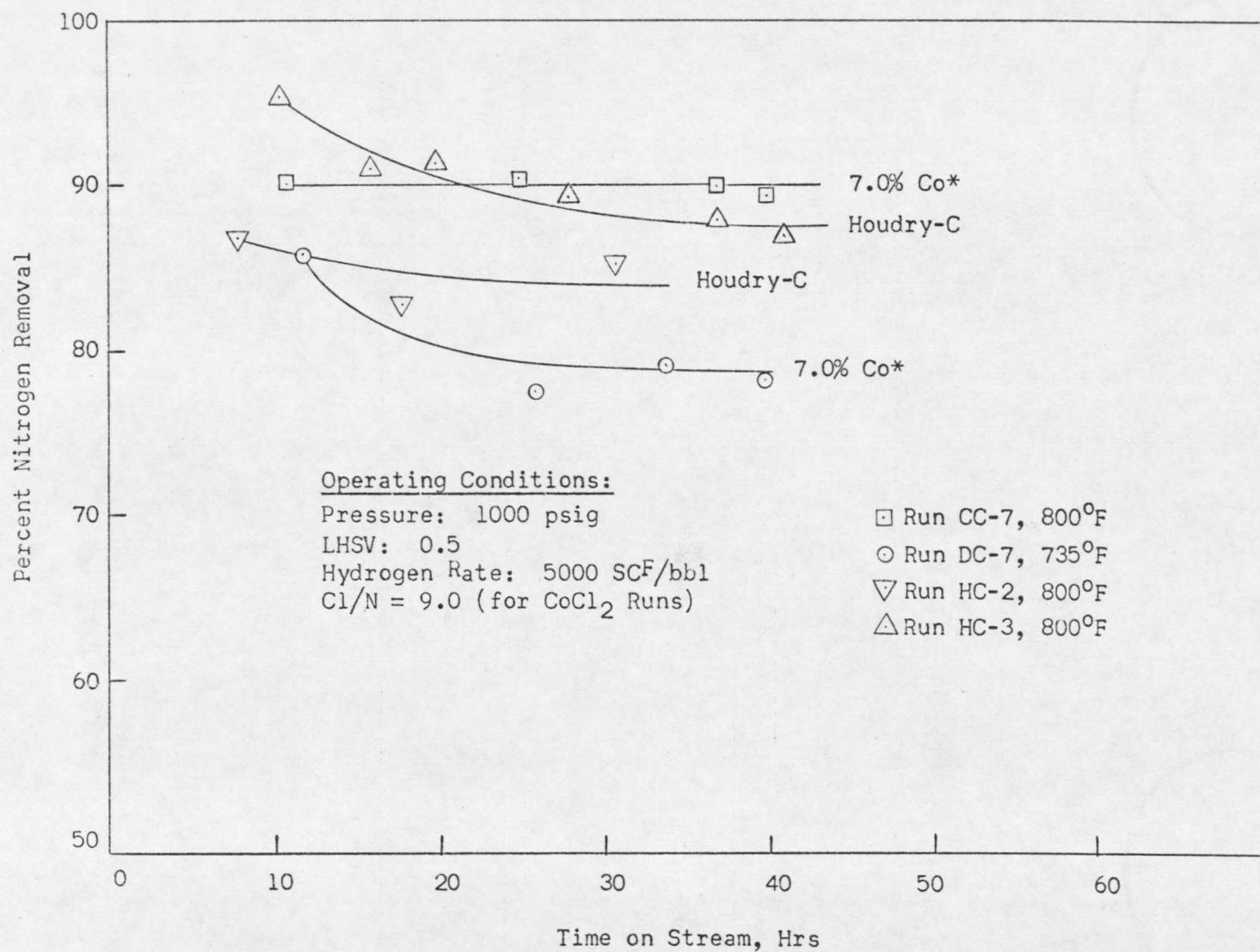


Figure 39. Comparison Between Cobalt Chloride and Houdry-C Catalysts.

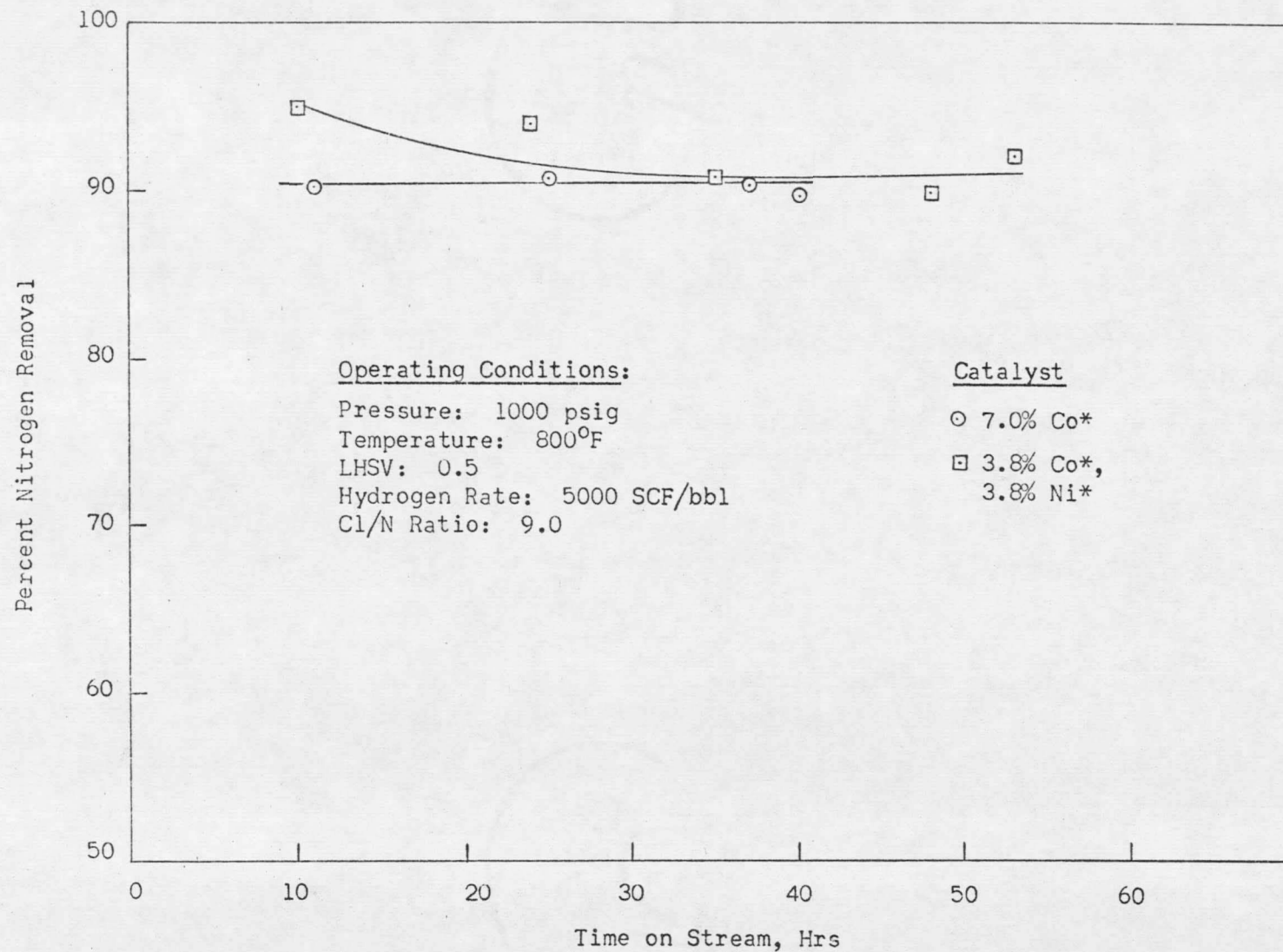


Figure 40. Comparison Between Cobaltous Chloride and Cobaltous-Nickelous Chloride Catalysts.

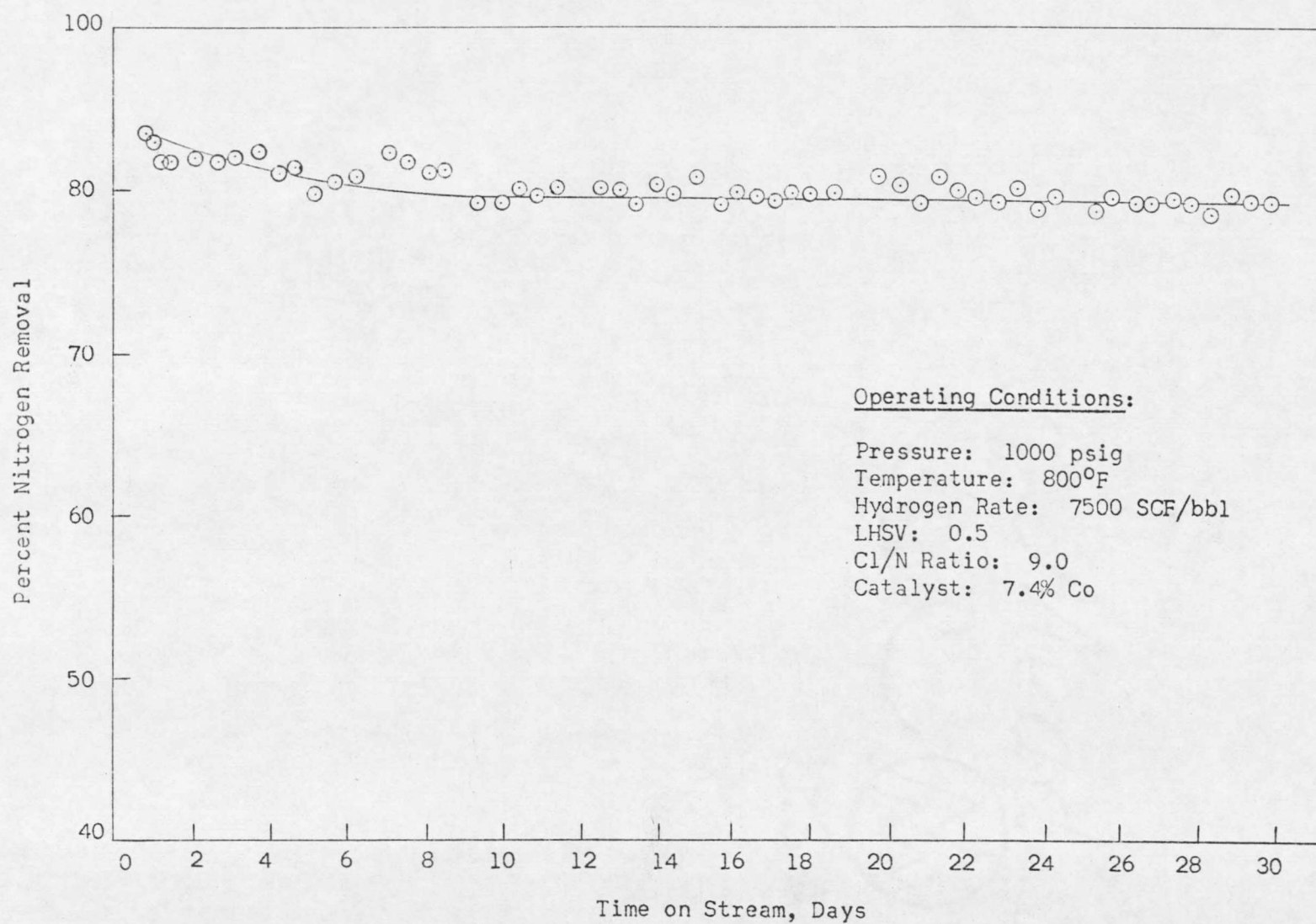


Figure 41. Nitrogen Removed as a Function of Time for an Extended Run.

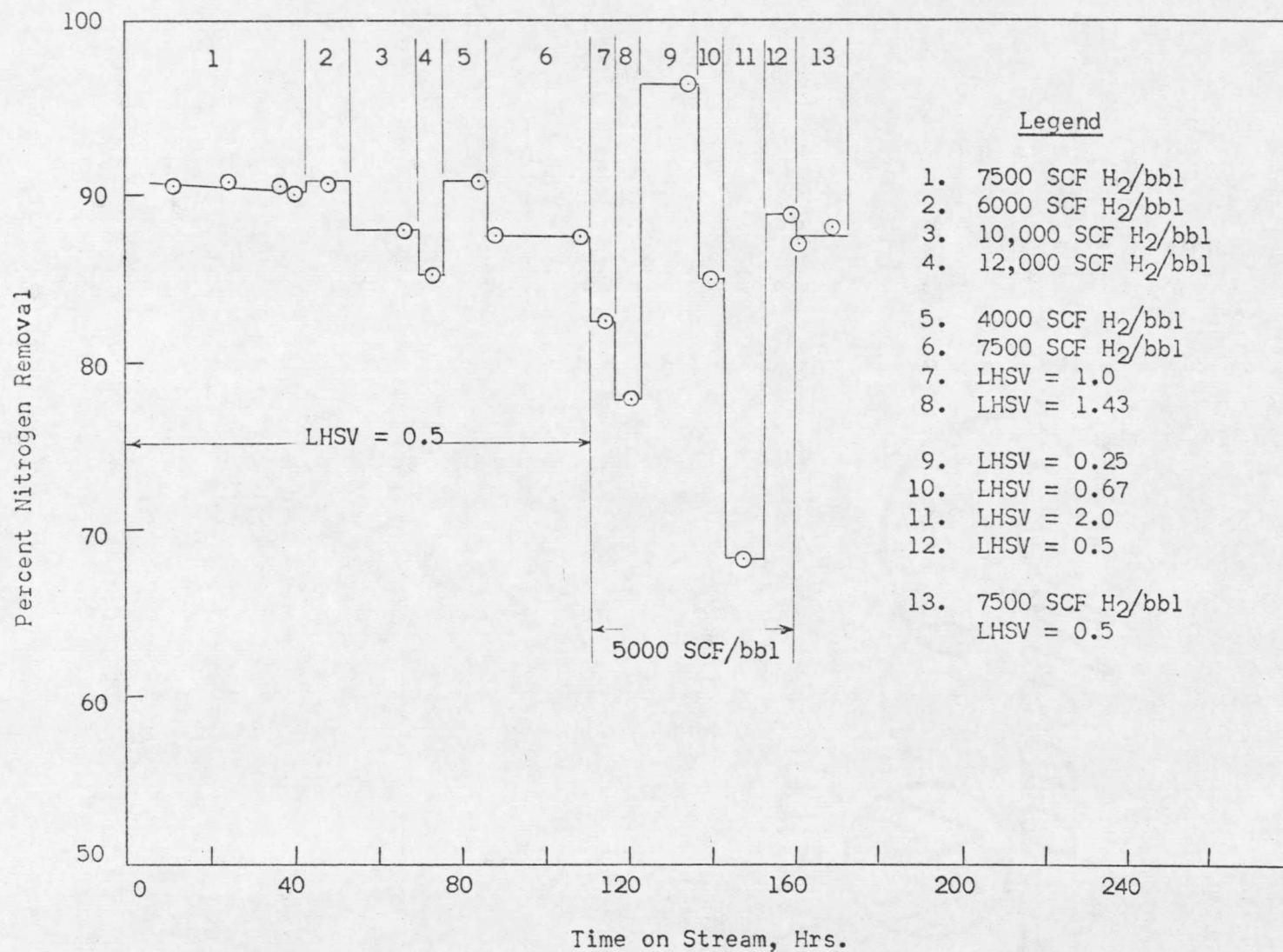


Figure 42. Effect of Changing Operating Conditions on the Hydrodenitrogenation Catalyst Activity.

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Cobaltours chloride as

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