



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

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

The hydrodenitrogenation of a variety of nitrogen-bearing compounds considered typical of those found in petroleum was carried out in a continuous flow system over a NiCl_2 -gaseous HCl catalyst. The extent of denitrogenation of aniline, quinoline, pyridine, pyrrole, indole, and indoline was determined when reactor temperature was varied between 450°C and 220°C at a constant space velocity of 1.0 and when space velocity was varied between approximately .5 and 3.0 at a constant temperature of 370°C all at a hydrogen pressure of 875 psig. From these runs it was apparent that aniline was the easiest compound to remove, followed by pyridine and quinoline which were approximately equal, then pyrrole, and finally indole and indoline.

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

The HCl atmosphere in the reactor, maintained by adding methylene chloride to the feed, not only increased the acidity of the alumina catalyst, but also resulted in the nitrogen eventually leaving the reactor as NH_4Cl rather than NH_3 , the form usually occurring in denitrogenation systems. The anticipated form of the active catalyst is as some NiCl_2 , HCl complex, possibly as the Friedel-Crafts acid $\text{H}^+(\text{NiCl}_3)^-$. After adsorption of the nitrogen onto the active catalyst sites, the reaction probably proceeds by the normal carbonium ion mechanism.

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February 14, 1973

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PETROLEUM HYDRODENITROGENATION CATALYST

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ALLAN REID FEDORUK

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ABSTRACT

The hydrodenitrogenation of a variety of nitrogen-bearing compounds considered typical of those found in petroleum was carried out in a continuous flow system over a NiCl_2 -gaseous HCl catalyst. The extent of denitrogenation of aniline, quinoline, pyridine, pyrrole, indole, and indoline was determined when reactor temperature was varied between 450°C and 220°C at a constant space velocity of 1.0 and when space velocity was varied between approximately .5 and 3.0 at a constant temperature of 370°C all at a hydrogen pressure of 875 psig. From these runs it was apparent that aniline was the easiest compound to remove, followed by pyridine and quinoline which were approximately equal, then pyrrole, and finally indole and indoline.

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

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as NH_4Cl rather than NH_3 , the form usually occurring in denitrogenation systems. The anticipated form of the active catalyst is as some NiCl_2 , HCl complex, possibly as the Friedel-Crafts acid $\text{H}^+(\text{NiCl}_3)^-$. After adsorption of the nitrogen onto the active catalyst sites, the reaction probably proceeds by the normal carbonium ion mechanism.

I. INTRODUCTION

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

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

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

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

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

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

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

II. RESEARCH OBJECTIVES

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

III. EXPERIMENTAL PREPARATION

A. EQUIPMENT

Several exploratory runs using the NiCl_2 catalyst system were made to become familiar with the apparatus. Initial indications were that equipment used on earlier studies would be satisfactory for this work; however, on beginning serious investigations, several problems arose which required the altering of the reactor system. With a major reaction product being ammonium chloride, below its sublimation temperature of 340°C , it collected as a solid at the reactor outlet. As there was already a constriction in this zone of the reactor, the accumulation of even a small amount of NH_4Cl caused the reactor to plug. (in previous studies, the nitrogen had left the reactor as NH_3 gas so this situation was not present). Temporary control of this problem was achieved by putting a small heating unit around the constriction to maintain the temperature above 340°C ; however, it was eventually decided that the reactor should be modified to better accommodate the NH_4Cl accumulation. A schematic diagram of the over-all reactor system is shown in FIGURE 1.

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

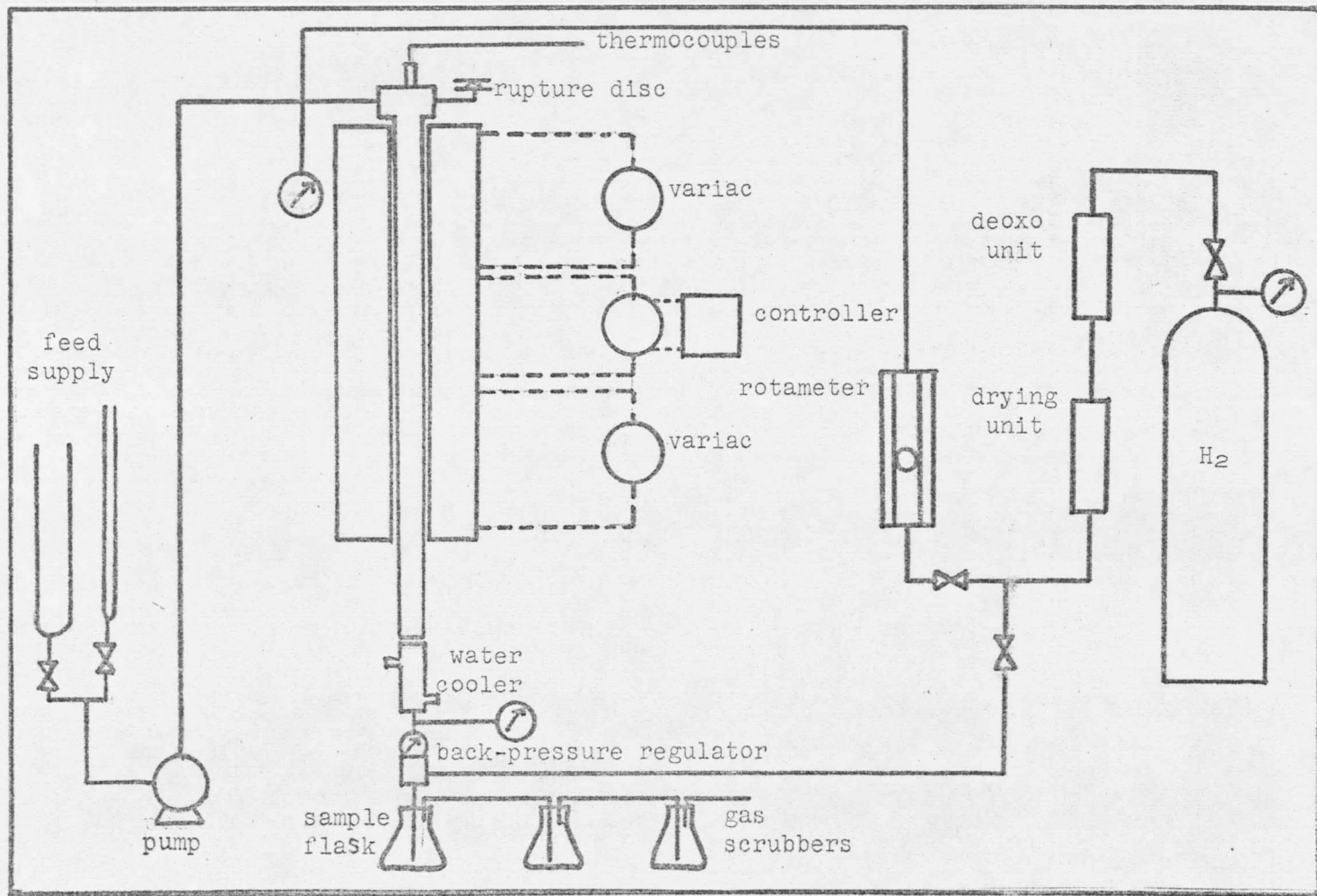


FIGURE 1: Schematic Diagram of Reactor System

controller using an iron-constantan thermocouple. This thermocouple plus three others were mounted in a stainless steel thermowell running axially through the catalyst bed. The heating section was then encased in a 12 inch diameter can packed with Zonelite insulation. The lower 21 inches of the pipe, which was not heated, served as a collecting section for the NH_4Cl . A detailed diagram of the reactor is presented in FIGURE 2:

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

B. REACTION MATERIALS

With the intent of this research being to study a variety of nitrogen compounds, it was decided to run those compounds shown in FIGURE 3 through the NiCl_2 -gaseous HCl denitrogenation system, these compounds being considered both typical of those found in petroleum and readily available from commercial suppliers. As a carrier for the nitrogen

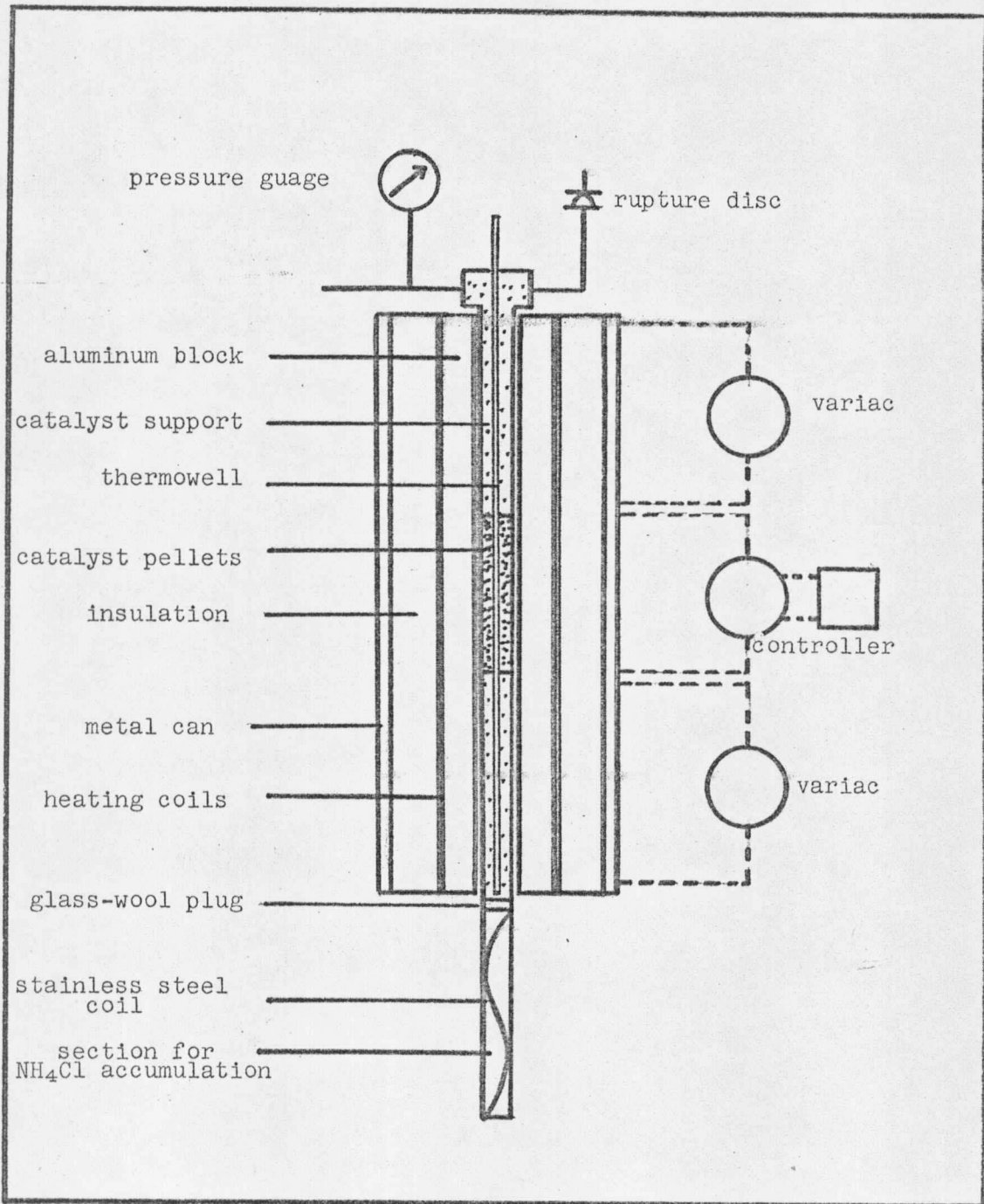


FIGURE 2: Detailed Diagram of the Reactor

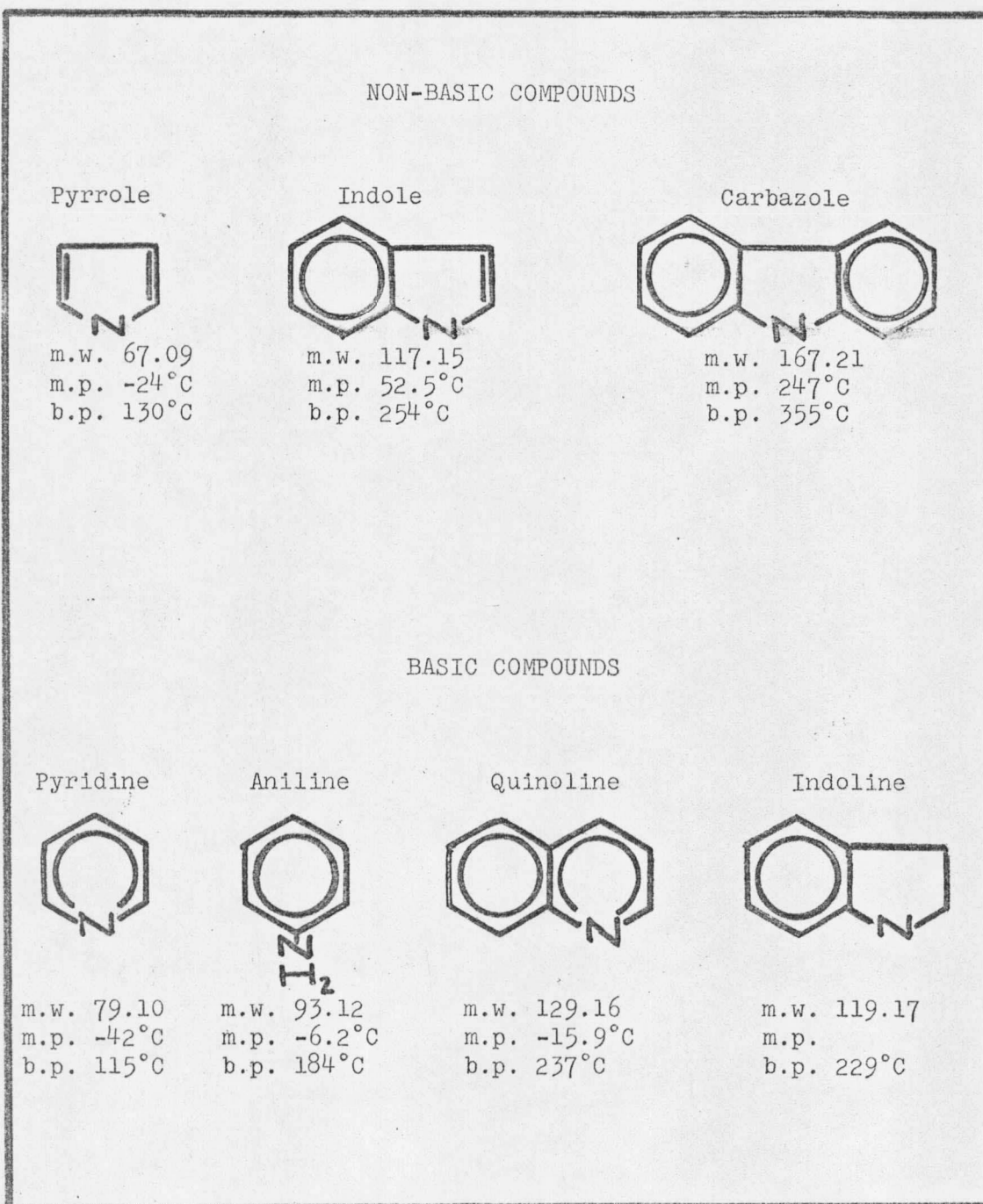


FIGURE 3: Typical Nitrogen Compounds Found in Petroleum

compounds, a high purity petroleum not affected by the hydrogenation process was desired. To this effect a mineral oil, "Penetec", supplied by the Pennsylvania Refining Corporation was used. Hydrogen was supplied by HR Oxygen Supply, Billing, Montana in 2000 psig cylinders. The HCl atmosphere in the reactor was maintained by adding methylene chloride to the liquid feed with the methylene chloride breaking down into HCl at reactor conditions.

C. CATALYST PREPARATION

The catalyst used was NiCl_2 impregnated on a Harshaw alumina catalyst pellet, the properties of the support being listed in TABLE 3. The approximate amount of NiCl_2 to be used in preparing the catalyst was calculated on the basis of the catalyst pellet pore volume while the exact catalyst composition was determined gravimetrically. The catalyst pellets as supplied by the Harshaw Chemical Company were dried at 420°F for 24 hours, then a solution of 60 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /100 ml water was prepared and poured over the pellets until they were completely immersed. This mixture was allowed to stand for 24 hours with periodic agitation to insure that the maximum amount of the NiCl_2 solution was absorbed. The excess solution was then decanted, the wet pellets spread over a blotter and allowed to air dry for 24 hours. After this drying, the pellets were stored until the reactor was to be charged. Prior to charging the reactor, 100 ml of the pellets were placed in an

oven at 420°F for 24 hours to remove the water of hydration. Nickel content of the pellets was determined to be 7.72% on the basis of the weight difference between the impregnated oven-dried pellets and the unimpregnated oven-dried pellets. By preparing a 5000 ml batch of pellets and only using 100 ml per run, a constant catalyst composition was maintained for all runs and thus catalyst composition could be eliminated as a variable for the purpose of data evaluation.

D. CHARGING THE REACTOR

In charging the reactor, the inlet fitting and thermowell were first sealed in place with teflon tape and copper anti-seize compound, the reactor inverted and 140 ml of inert dry alundum catalyst support poured into the stainless steel pipe. This was followed by 100 ml of the dry NiCl_2 catalyst pellet and then another 110 ml of the catalyst support, the inert support serving to center the catalyst pellets relative to the heated aluminum block. This pellet section was separated from the NH_4Cl condensation section by a plug of glass wool which was in turn supported by a coil of stainless steel tubing. The outlet fitting was then screwed in place and the reactor lowered into the heated aluminum block. All inlet and outlet lines were connected, again using teflon tape to seal them, and the reactor pressure tested at 1000 psig. After the reactor had reached the desired temperature, the run was begun.

E. INITIAL OPERATING CONDITIONS

McCandless (12) reported a high percentage of nitrogen removal for a NiCl_2 -gaseous HCl catalyst system with operating conditions of 800°F, 1000 psig, and a Cl/N ratio of 9.4. Since the effect of space velocity and temperature on nitrogen removal was to be studied, it was decided to operate the reactor at something less than the high removal conditions given above, in the hope that differences in percent removal of nitrogen would then be more discernable. From the analysis of the data presented by McCandless, it was decided that these reduced conditions would be 700°F, 875 psig pressure, and a Cl/N ratio of 8.6.

F. INITIAL EXPERIMENTAL RUNS

Anticipating that a catalyst line-out time would be required on all experimental runs, two initial runs were undertaken to determine what this time should be. Using the Penetec feedstock with .315% nitrogen (pyridine), the reactor was run for 30 and 36 hours, the operating conditions and results presented in FIGURE 4. One run was also made with the hydrogen rate as a variable since at too low a hydrogen rate, the reaction itself would cease to be the controlling step, diffusion instead controlling the rate of reaction. FIGURE 5 shows the results of this run. Four runs, as indicated in FIGURE 6, were also made using a catalyst of varying Ni content to determine the optimum Ni content for the catalyst support.

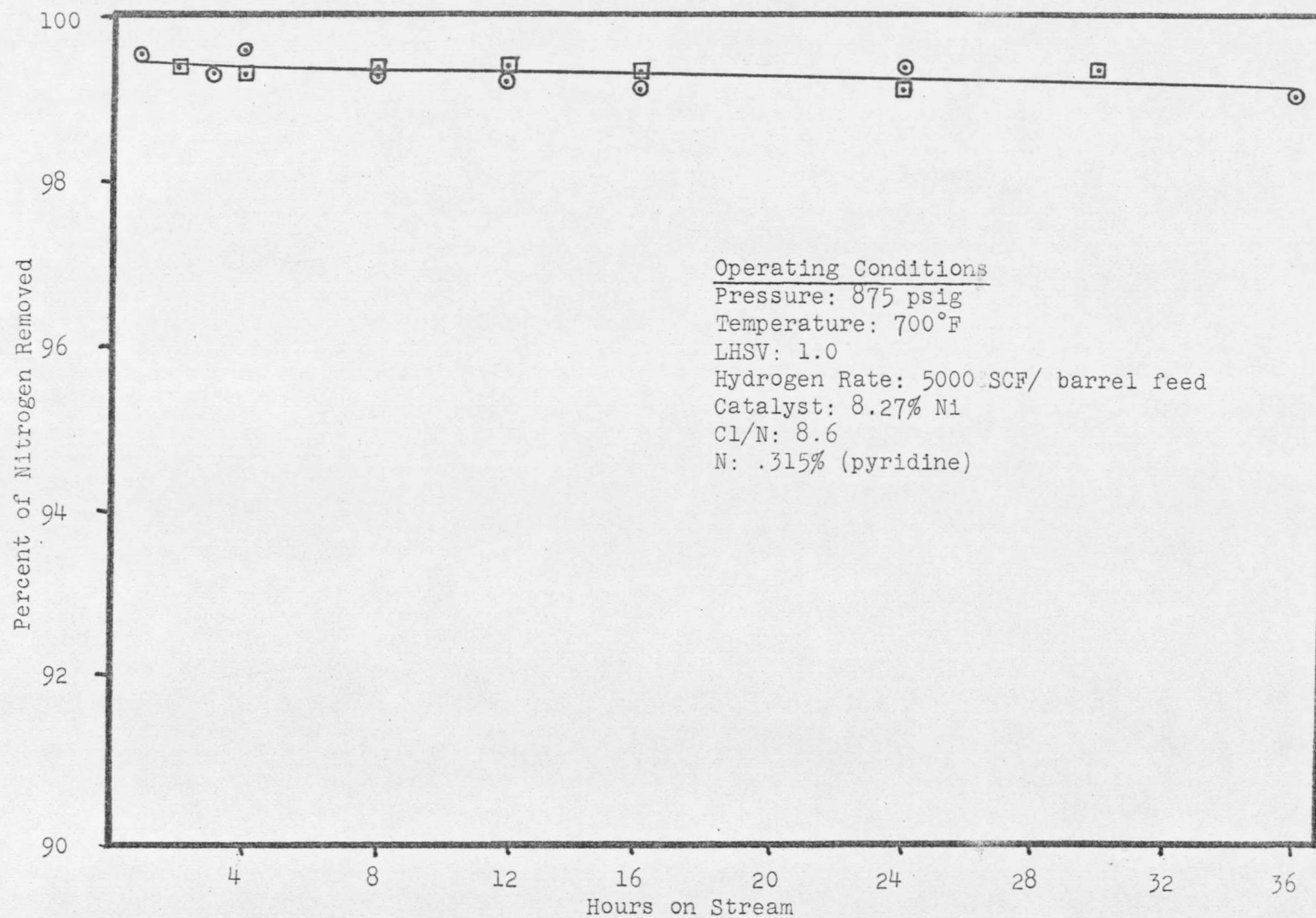


FIGURE 4: Time Requirement for Catalyst Line-out

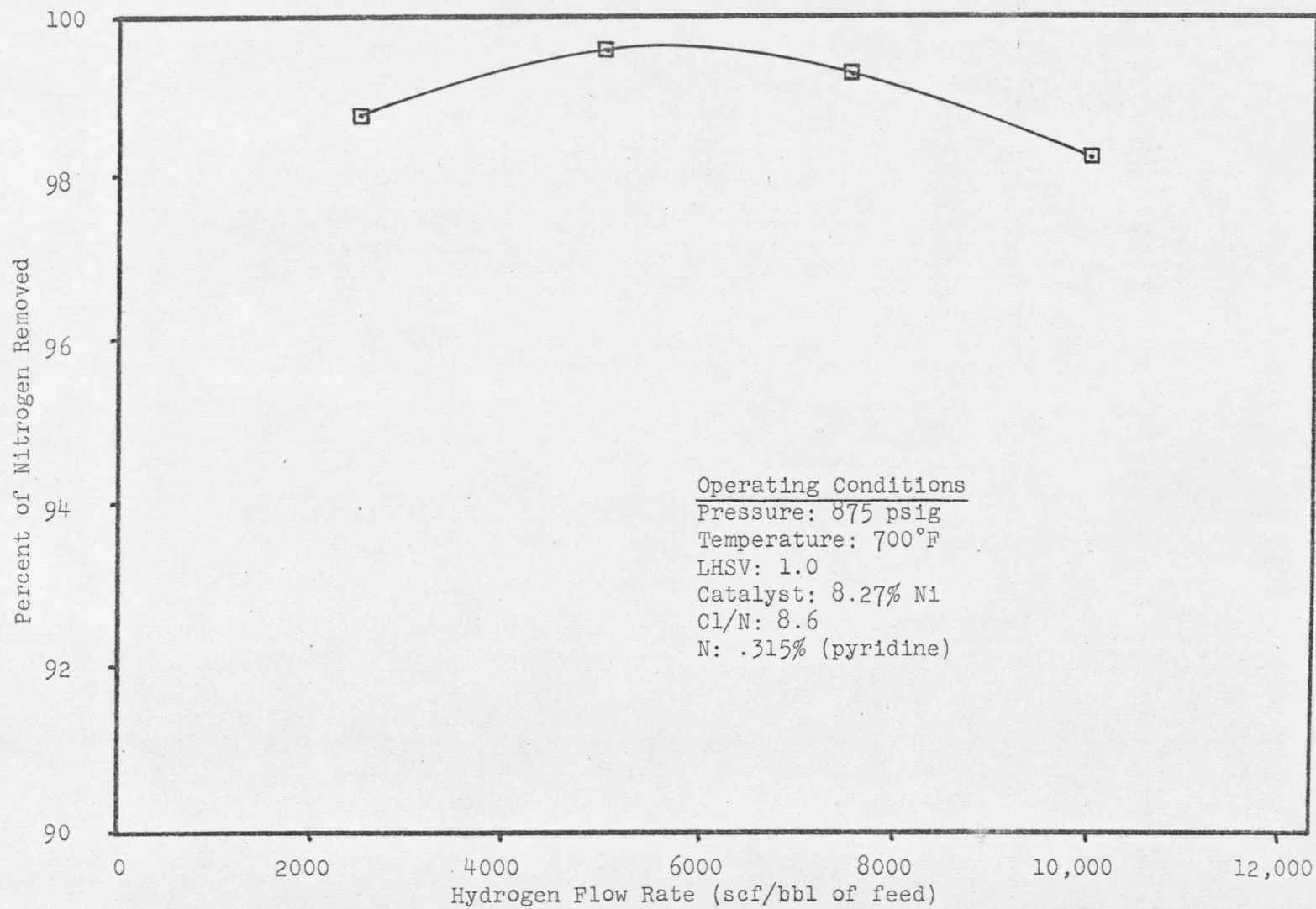


FIGURE 5: Optimum Hydrogen Flow Rate

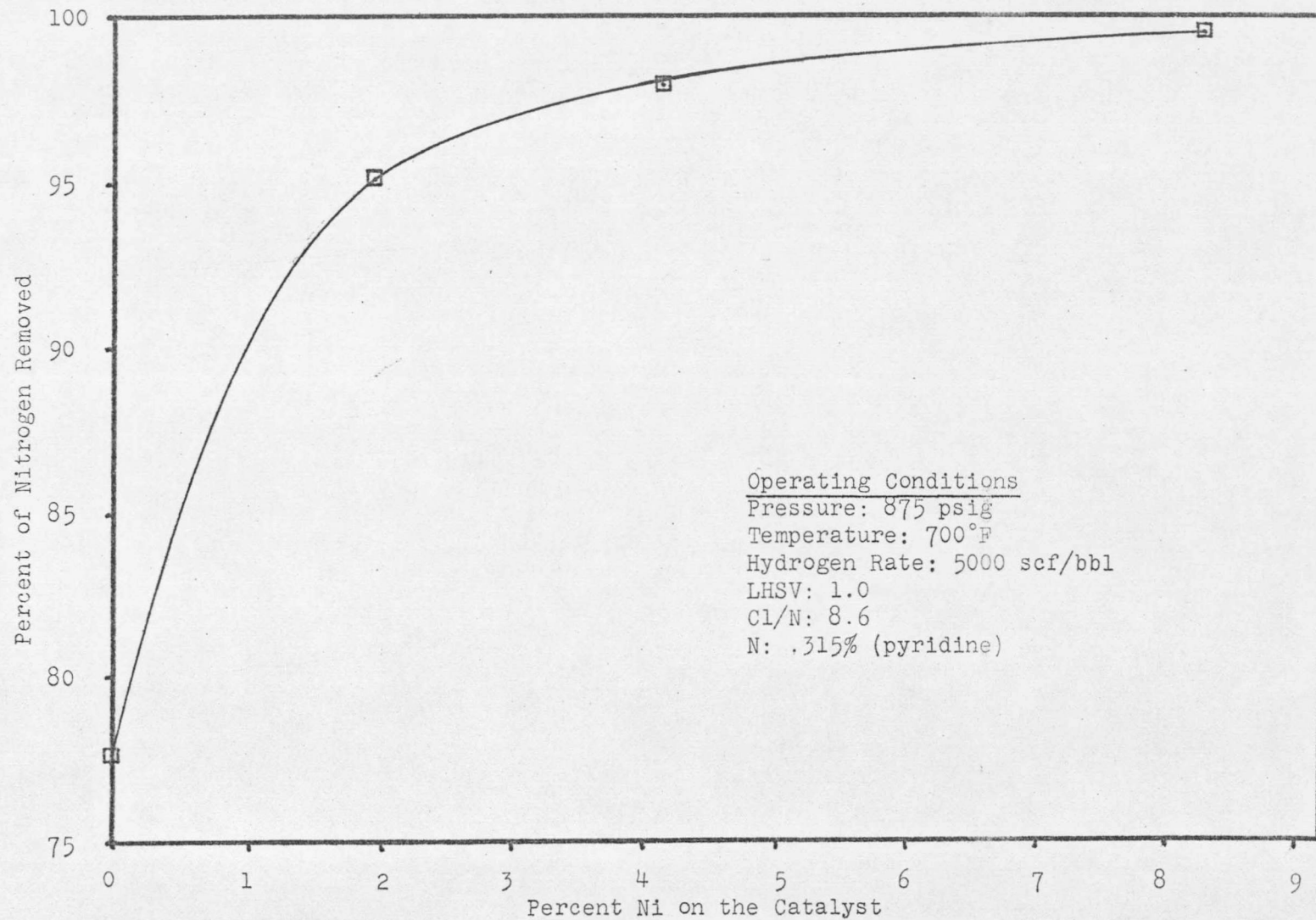


FIGURE 6: Optimum Ni Content on the Catalyst

G. PURE COMPONENT RUNS

To study the kinetics of various nitrogen compounds, runs using the compounds shown in FIGURE 3 were attempted, to correlate nitrogen removal and liquid hourly space velocity (LHSV). A problem arose in preparing the carbazole feed in that carbazole, a solid, was not sufficiently soluble in the Penetec, methylene chloride feed to allow pumping through the reactor system. Attempts to dissolve the carbazole in benzene, ethanol, carbon tetrachloride, isopropyl cyclohexane, and 1-methyl naphthalene prior to mixing with the Penetec and methylene chloride all proved unsuccessful so no runs were made using carbazole as a nitrogen compound. The results and operating conditions for the remainder of the runs, that is with aniline, quinoline, pyridine, pyrrole, indole, and indoline are shown in FIGURE 7. A series of runs to determine the effect of reactor temperature on nitrogen removal for these same compounds was also made. FIGURE 8 represents these runs.

H. PRODUCT ANALYSIS

A minimum of two Kjeldhal analyses were performed on each petroleum sample following the procedure outlined by Lake and coworkers (10). Because of the low nitrogen content of the product, approximately two gram samples were used in the digestion phase and ultimately titrated with a .00797N standard sulfuric acid solution. Pre-weighed packages of a $\text{HgO-K}_2\text{SO}_4$ mixture especially designed for Kjeldhal analyses were obtained from Matheson Scientific and proved very successful.

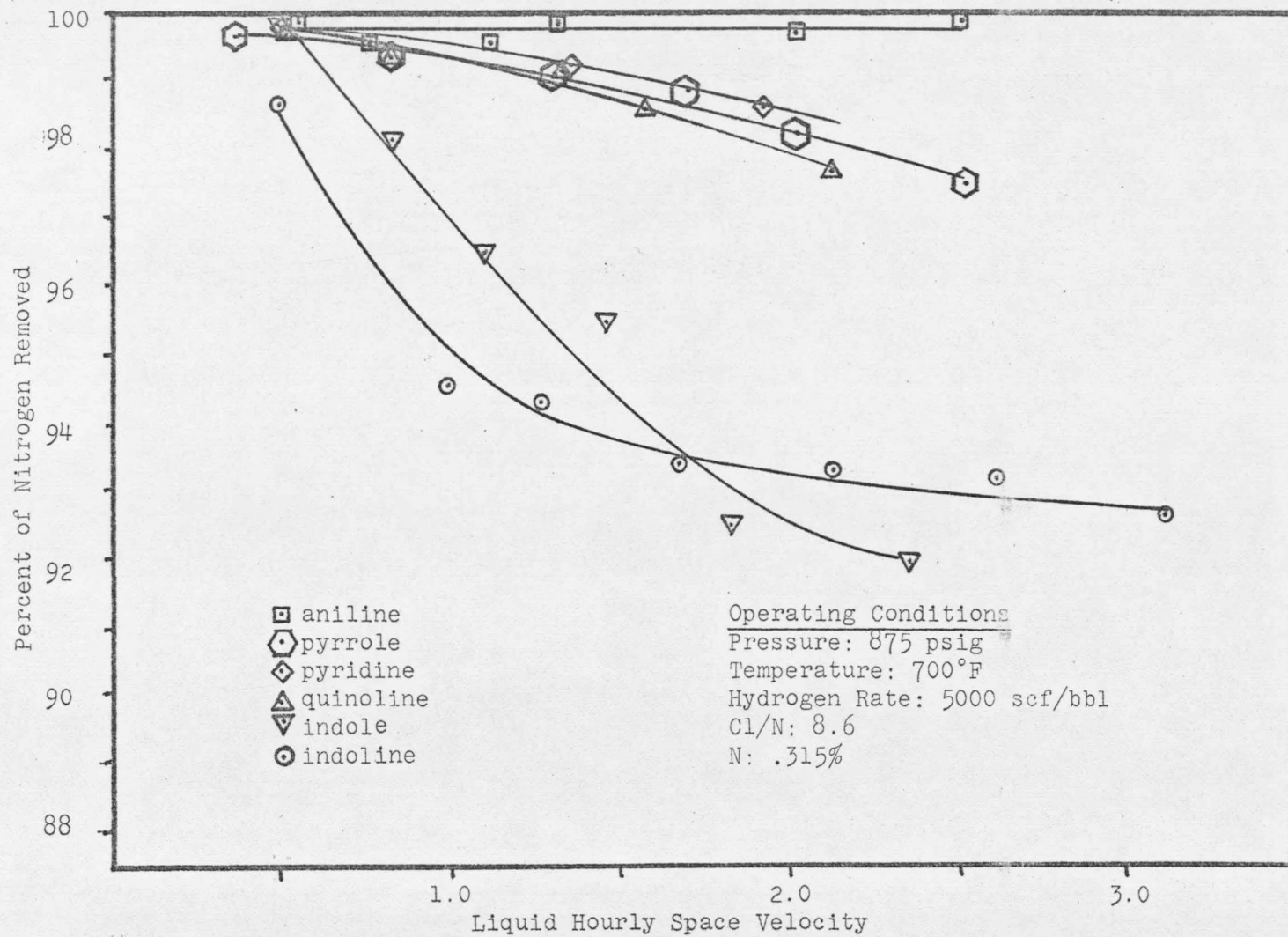


FIGURE 7: Effect of Space Velocity on Nitrogen Removal

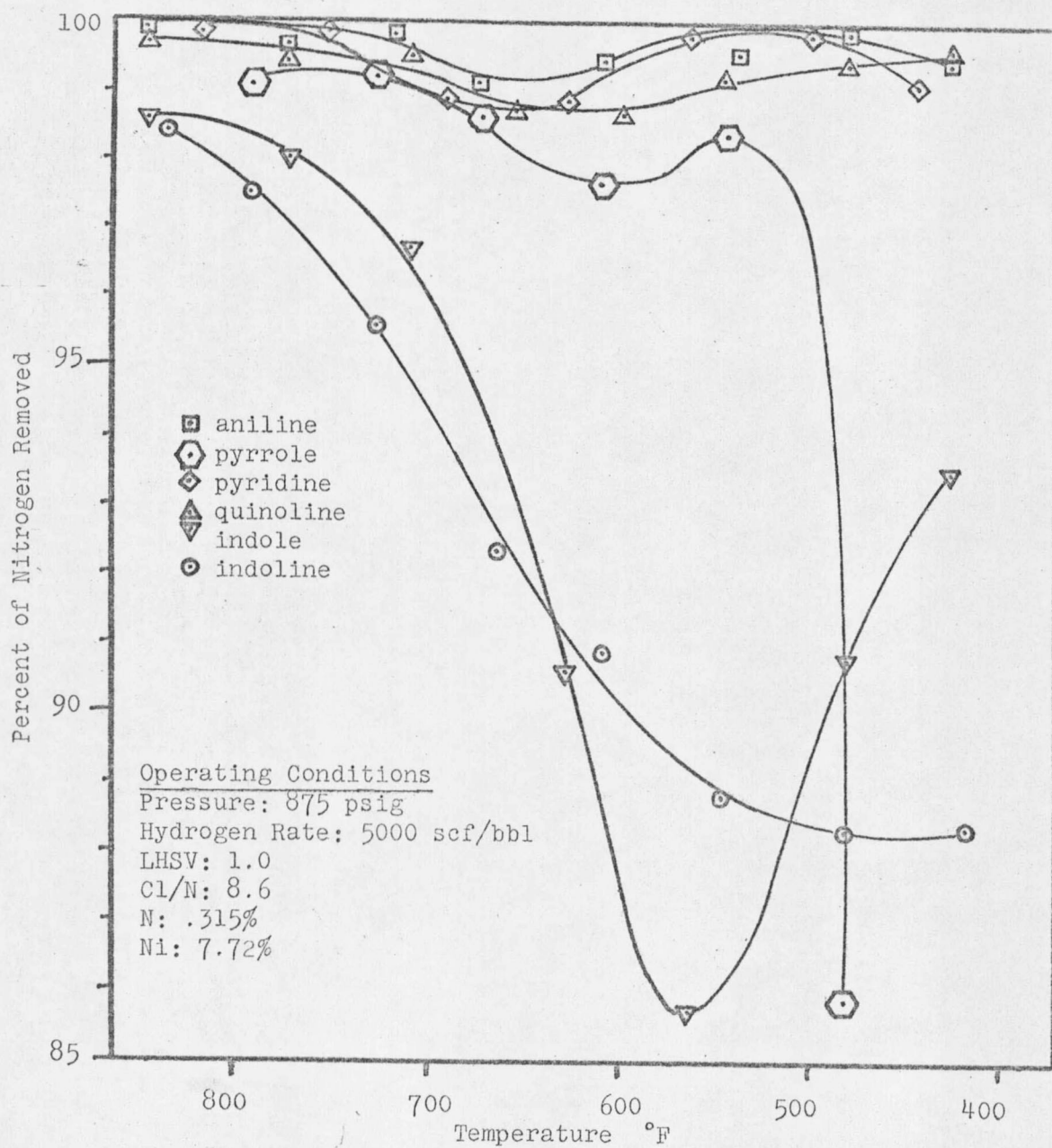


FIGURE 8: Effect of Reactor Temperature on Nitrogen Removal

IV. RESULTS AND DISCUSSION

A. INITIAL EXPERIMENTAL RUNS

1. Line-out Time

The view that a catalyst line out time is required was apparently incorrect as can be seen from FIGURE 4. While a slight decrease in catalyst activity may occur over the length of the two runs, the sudden drop in activity anticipated during the first few hours of operation did not occur. Regardless, a line-out time of 10 ml feed/ml catalyst was allowed to insure that the system was stable before a sample was taken. Similarly, a line-out time after changes in operating conditions was also anticipated. That is, whenever, the temperature, pressure, or space velocity of the system was changed it was felt that a definite line-out time was required to allow the system to come to equilibrium before a meaningful sample could be taken. In this respect, reference was made to work done by Whitcomb (24) using a cobaltous chloride-gaseous HCl catalyst system operating under almost identical conditions where a line-out time of 4 ml feed/ml catalyst was established. With this in mind, a 6 ml feed/ml catalyst line-out time between changes in operating conditions was chosen.

2. Diffusion

The transport of the reactants from the bulk fluid to the catalyst pellet and similarly the transport of the products from the catalyst to the bulk fluid can, without the proper selection of conditions, be the

rate controlling step in the catalytic reaction (18). To be sure that the data being collected reflected the characteristics of the actual chemical reaction occurring and not the diffusion step mentioned above, a run was made to establish a hydrogen flow rate such that diffusion would not be the rate-controlling step in the over-all reaction. As can be seen from FIGURE 5, at hydrogen rates between 3000 and 9000 scf/bbl, nitrogen removal was 99% or greater while at the lower and higher rates, nitrogen removal was less effective.

While the increase of nitrogen removal with increasing hydrogen rate was anticipated and is due to the decreasing effect of film diffusion, the drop in conversion at the high hydrogen rate is unusual. It may be that at these high rates (9000 scf/bbl of feed and above) that channeling develops in the catalyst bed thereby reducing the effectiveness of the system. As a result, a hydrogen rate of 5000 scf/bbl of feed was chosen for the remainder of the runs.

3. Nickel Content on Catalyst

To determine the best level of Ni on the catalyst support, four runs were made with different catalyst compositions for each run. After a substantial increase of catalyst activity when the nickel content was increased from 0 to about 2 %, see FIGURE 6, the activity tended to level off. At a nitrogen removal of about 99% the Ni content of the catalyst was approximately 7 %. To eliminate nickel content as a var-

iable for subsequent runs, a 5000 ml batch of catalyst was prepared with a 7.72% Ni content and was used for the remainder of the experimental runs.

B. PURE COMPONENT RUNS

1. Liquid Hourly Space Velocity (LHSV) as a Variable

a. Empirical Rate Equation

Six runs were now made using aniline, quinoline, pyridine, pyrrole, indole, and indoline as the nitrogen-bearing compounds. The reactor was operated between space velocities of approximately .5 and 3.0, as indicated in FIGURE 7, and an attempt made to determine the reaction order and rate constants for the denitrogenation of the petroleum feed from the data collected.

For a general reaction of the type:



the rate equation can be written as:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = z k C_A^a C_B^b \quad 1.$$

where r is the reaction rate, C_A and C_B are the reactant concentrations, a and b are constants, and z is a catalyst factor to account for preparation, composition, and physical properties of the catalyst.

Several simplifications can be made in this equation. Since the catalyst composition and preparation is the same for all the test runs, z , the catalyst factor is constant and can, therefore, be combined with

the rate constant to give:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k_1 C_A^a C_B^b \quad 2.$$

Since one of the reactants, hydrogen, is present in a large excess during the reaction, it experiences a negligible change in concentration and can similarly be considered constant and combined with the rate constant to give:

$$-r_A = -\frac{dC_A}{dt} = k_2 C_A^a \quad 3.$$

To further facilitate calculations, the concentration of nitrogen itself rather than the concentration of the nitrogen-containing compound was used in defining the rate to give:

$$-r_N = -\frac{dC_N}{dt} = k_3 C_N^n \quad 4.$$

By letting A be the original amount of nitrogen present and x be the amount converted, the rate equation can be integrated by the separation of variable to give:

$$\int_0^x \frac{dx}{(A-x)^n} = k_3 t \quad 5.$$

where t is the contact time. Since t is rather difficult to determine, its reciprocal, space velocity, with units of milliliters of feed per milliliter of catalyst per hour is substituted for t, thus giving:

$$\int_0^x \frac{dx}{(A-x)^n} = \frac{k}{Sv} \quad 6.$$

where once again n is the order of the reaction.

b. Data Evaluation

Applying the integral method of data evaluation requires that various values of n be substituted into equation 6, and a check made to see if there is agreement between the data and the assumed rate expression. Assuming then a reaction order of zero, the rate expression becomes:

$$\int_0^x \frac{dx}{(A-x)^0} = \frac{k}{Sv} \quad \text{or} \quad 7.$$

$$x = k/(Sv \cdot C_{A0}) \quad 8.$$

implying that the rate of conversion is independent of the concentration. A plot of x versus $1/Sv$ should then be a straight line with slope k/C_{N_0} if the reaction is zero order. Such a plot is presented in FIGURE 12 for all six nitrogen compounds tested.

For a first order reaction, equation 6 becomes:

$$\int_0^x \frac{dx}{(A-x)^1} = \frac{k}{Sv} \quad \text{or} \quad 9.$$

$$\ln \frac{A}{(A-x)} = \frac{k}{Sv} \quad 10.$$

so a plot of $\ln A/(A-x)$ versus $1/Sv$ should yield a straight line of slope k for any data which follows first order kinetics. FIGURE 13 is a check for first order kinetics.

In a second order reaction, $n=2$, and the general rate expression is:

$$\int \frac{dx}{(A-x)^2} = \frac{k}{Sv} \quad 11.$$

which integrated gives:

$$\frac{1}{(A-x)} - \frac{1}{A} = \frac{k}{Sv} \quad 12.$$

so a plot of $1/(A-x)$ versus $1/Sv$, FIGURE 14, would give a straight line of slope k and intercept $1/A$ for a denitrogenation reaction following second order kinetics.

On the basis of these plots, the approximate reaction order for the various nitrogen compounds was established. Aniline appears to be zero order with the scatter present when testing for first and second order being so extreme that no meaningful curve could be drawn. The plot of the indole data fit the first order expression well while indoline seemed to have both zero and first order tendencies. Quinoline, pyridine, and pyrrole approach second order kinetics though there still was a distinct curve in the plot. As is apparent from the preceding discussion, the integral method provides only an approximate indication of the order of the reaction. The problem is that the n value substituted into equation 6 need not be an integer, so fractional orders are possible, making this trial-and-error curve fitting procedure very tedious. An alternate to this is the differential method of analyzing the data.

Looking again at equation 4:

$$-r_N = - \frac{dC_A}{dt} = k_N C_N^n \quad \text{or} \quad 4.$$

$$\ln \left(- \frac{dC_A}{dt} \right) = \ln k + n \ln C_N \quad 13.$$

The procedure then is to plot C_A versus t , or $1/Sv$, and determine the slope of this curve at various points. A plot of the natural logarithm of this slope versus \ln of the concentration will give a straight line of slope n with the intercept at $\ln k$. The differential analysis of the data appears in FIGURE 15 through FIGURE 20, with the results listed in TABLE I.

TABLE I: Differential Analysis of LHSV Data

Compound	Reaction Order	k
Aniline	0	0
Indole	.97	.61
Indoline	1.22 / 4.66	1.26
Quinoline	1.63	.77
Pyridine	2.43	.44
Pyrrole	2.82	.56

With the large differences apparent in the reaction orders of the nitrogen compounds, it is difficult to make any comparison of the reactivity on the basis of the k values. It would be safest to say only that a simple mechanism is not going to account for these differences and a multi-step reaction should be anticipated. Some qualitative comments, however, can be made.

The zero order, zero k value of aniline is a result of its extreme susceptibility to denitrogenation. Throughout the range of LHSV's tested, aniline was essentially completely removed. This is not unexpected in that aniline is the only compound tested where denitrogenation does not require the breaking of some type of cyclic ring. Quinoline, pyridine, and pyrrole all exhibit approximately the same response to changing space velocity with a slight drop in conversion as space velocity increased. Indole and indoline are also similar in that for both, conversion drops off rather sharply then apparently levels out. The two n values given for indoline represent this sudden drop ($n=1.22$) and the subsequent leveling off ($n=4.66$).

2. Temperature as a Variable

a. General Catalyst Theory

With the implications of these results being vague, another set of runs was made where nitrogen removal was determined as a function of reactor temperature as presented in FIGURE 8. From the results of the variable space velocity and temperature runs, once again some qualitative conclusions can be drawn about the ease of removal of the various compounds tested. Aniline appears to be the easiest to remove followed by pyridine and quinoline. Pyrrole is the next easiest to remove followed by indole and indoline.

Before further discussing these particular results, a review of general catalyst theory is in order. The most common theory, "The Principle of Sabatier" states that unstable intermediates are formed between the catalyst and the reactants which then decompose in such a way as to regenerate the catalyst (3). The formation of these unstable intermediates reduces the energy barrier which must be surmounted in order for the reaction to proceed. It is this theory which will be followed in discussing the dual functional catalyst, NiCl_2 .

A dual functional catalyst is one which contains two types of activity (23) with the over-all reaction resulting from a sequence of successive reaction steps on or with the different catalytic centers. A typical hydrocracking catalyst will contain a metal such as platinum or nickel for hydrogenation, dehydrogenation activity and an acidic component in the form of Lewis or Bronsted acids for cracking activity. Nickel is a typical base metal that when distended on an acidic support is an effective hydrocracking catalyst. Its role in hydrocracking has been considered to be largely that of a hydrogenation component that protects acidic sites; that is, it keep the acidic sites clean and active through the hydrogenation of coke precursors (2). According to Voge (22), the mechanism for catalytic cracking is initiated with the aromatic adding a proton directly to become a carbonium ion. The highly reactive acid surface then causes rearrangement and dissociation of the carbonium ion with the release of an olefin. As a general rule for dual functional

catalysts, the reactions occurring on these acidic sites are rate limiting (2).

b. Interpretation of Data

Usually these catalysts are poisoned by nitrogen compounds of the type investigated in this project, with the less basic compounds supposedly not inhibiting catalyst reactivity quite as strongly as the more basic compounds (22). Since a difference in reactivity was observed for the nitrogen compounds tested over the NiCl_2 system, a check was made to see if any correlation existed between basicity, measured as a pKa value, and reactivity for this system. The pKa value, the measure of the affinity of a base for a proton, is calculated from the following equation:

$$K_a = \frac{[\text{H}^+][\text{B}]}{[\text{BH}^+]} \quad 14.$$

where the lower the pKa value, the more acidic the compound. Values for most of the compounds tested are presented in TABLE 2 (14).

Compounds	pKa Values
Pyridine	5.3
Quinoline	4.9
Aniline	4.6
Pyrrole	0.4
Indole	-2.3

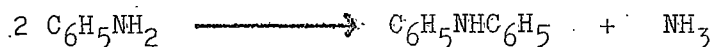
It appears from this that basicity does play an important part in determining the ease with which the nitrogen compounds are removed.

Aniline, quinoline, and pyridine are all removed relatively easily as is apparent from the conversion versus temperature run, FIGURE 8, and all have approximately equal pKa values. Pyrrole with a pKa value of 0.4 is the next most difficult to remove while indole with the lowest pKa value is the most difficult of the nitrogen compounds listed to remove.

The basicity of these compounds depends upon the extent to which the unshared electron pair on the nitrogen atom is available for interaction with other compounds. For example, in pyridine the electron pair occupies a plane trigonal orbital, the nitrogen atom is sp^2 hybridized, so the pKa of pyridine (pKa=5.3) is between that of an aliphatic amine such as triethylamine (pKa=9.7) where the unshared electron pair occupies a tetrahedral orbital and that of elementary nitrogen or a cyano compound where the unshared electrons occupy a pure s orbital (9). In pyrrole the two lone electrons of the ring nitrogen are incorporated into the π layer. Forming part of the aromatic sextet, these electrons are not readily available for salt formation; therefore, a high concentration of hydrogen ions is required to bring about protonation of pyrrole, resulting in its pKa value of 0.4. Similarly with indole, the lone pair of electrons from the nitrogen is an integral part of the π electron system and as such is not readily available for salt formation.

The significance of the basicity of these compounds in relation to their reactivity lies in the nature of the activity of the catalyst

pellet. Ogasawara and coworkers (15) suggested that the pre-treatment of an alumina catalyst pellet with liquid HCl results in an increase of the Lewis acidity of the catalyst. Undoubtedly then, the HCl atmosphere maintained over the NiCl₂ catalyst bed used here would also serve to increase the Lewis acidity of the pellets. With a Lewis acid being an electron acceptor, the interaction between the lone electron pair of the nitrogen atom of the compounds tested and the Lewis acid sites on the catalyst is a distinct possibility. From the order of reactivity presented previously it may even be speculated that this interaction between the electron pair on the nitrogen atom and the Lewis acid sites on the catalyst may be the rate controlling step of the reaction. In fact, Ogasawara (15) concluded in his study of the synthesis of diphenylamine over HCl treated alumina, that in the reaction:

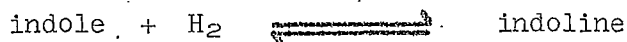


that the rate-determining step was the adsorption of the aniline.

Strictly on the basis of pKa values, the reactivity of aniline should be slightly less than that of pyridine and quinoline while in fact it appears to be slightly greater. Since complete nitrogen removal for heterocycles must eventually involve some hydrogenation and cracking steps, the breaking of the single C-N bond in aniline should be easier than the breaking of the cyclic rings present in the other compounds and probably accounts for its added ease of removal. This

may then imply that ring hydrogenation and cracking also has an effect on the reaction rate.

The similarity of the indole, indoline curves is very puzzling. While no pKa value is available for indoline, it is known to be more basic than indole (as an analogy, the pKa of pyrrole is .4 while that of its hydrogenated counterpart pyrrolidine is 11.3) and as such should be more reactive than indole, not less. One possibility is that the basicity of indoline is so high that it in fact acts as a catalyst poison to inhibit catalyst reactivity. Another is that an equilibrium exists between indole and indoline as suggested by Adkins and Coonradt (1) from their investigations on the selective hydrogenation of nitrogen compounds such that:



and that "...even at pressures of about 250 atm. the indole is present in the equilibrium mixture in rather considerable amounts." Noting the lower reactivity of pyrrole in FIGURE 8, perhaps five membered rings in general are more difficult to remove though no reason for this can be offered.

The most obvious conclusion from the similarity of the indole, indoline curves is that for these two compounds at least, basicity is not solely rate controlling. Also, since indole is known to hydrogenate to indoline under conditions less severe than those imposed here (19),

hydrogenation is not the rate controlling step in the denitrogenation. This may also be inferred from looking at the resonance of the various compounds. One would expect that if hydrogenation were rate controlling, the compounds with the higher resonance energies would be less reactive; however, this correlation does not exist.

If hydrogenation of the heterocyclic ring is not rate controlling and neither is the breaking of the nitrogen-benzene ring bond (as evidenced by the high reactivity of aniline), then probably the cracking step of the hydrogenated heterocyclic ring controls the rate. Thompson and coworkers (21) found the end products of the catalytic denitrogenation of indole to be ethyl cyclohexane, of quinoline to be n-propyl cyclohexane, and of pyridine to be n-pentane. If this is true for the NiCl_2 system investigated here, then the cleavage of the C-N bond in the heterocyclic ring probably greatly influences the rate. This is what McCandless (12) speculated in stating "...that cracking of the C-N bonds is the rate-determining step..." in his study of the NiCl_2 -gaseous HCl catalyst system. This step though cannot account for the difference in reactivity between quinoline and indole, with their most prominent difference being pK_a values. As evidenced by the peculiar shapes of the curves in FIGURE 8, it may be that both adsorption and C-N bond cracking influences the rate, with reactor conditions determining the extent of this influence.

C. REACTION INTERMEDIATES

The conventional carbonium ion reaction mechanism, referred to earlier, when applied to a hydrodenitrogenation reaction with indole would result in a reaction as presented in FIGURE 9 below.

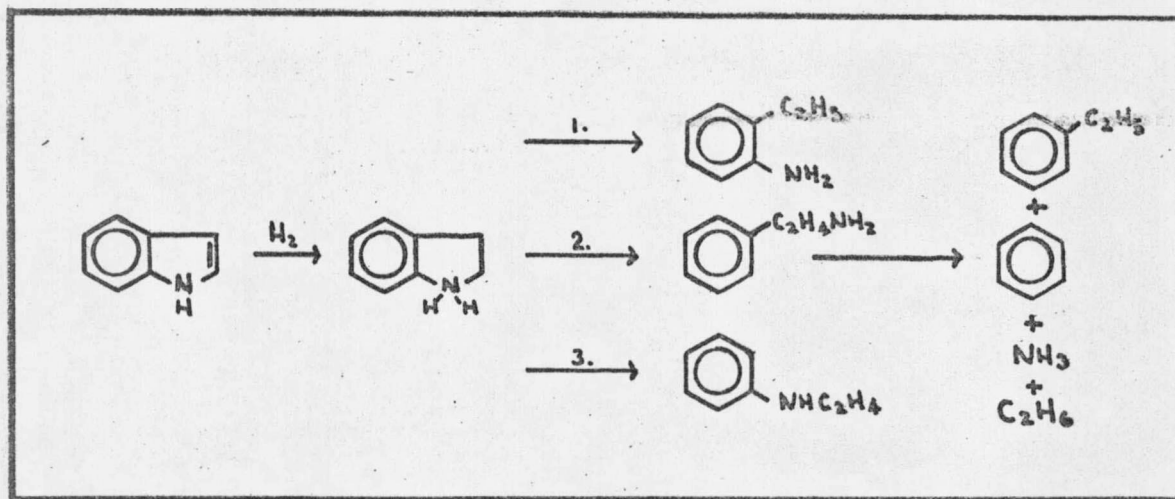
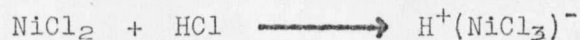


FIGURE 9: Conventional Carbonium Ion Reaction Mechanism

where sequence 1. is the most likely to occur, followed by 2. and then 3. The exact form of the catalyst-reactant complexes occurring during the reaction can only be speculated. From the behavior of the system with increasing Ni content, see FIGURE 6, and from the effect of increasing the Cl/N ratio in the feed (12), it appears that some form of a NiCl₂ adsorbed HCl complex is the most probable form for the catalyst.

The reaction of HCl with NiCl₂ by the reaction:



could produce a Friedel-Crafts acid which could then conceivably exhibit

both the acidity for cracking and the metal activity for hydrogenation to result in hydrodenitrogenation (25). Tanaka and Ogasawara (20) in their study on the adsorbed state of aniline on HCl-treated alumina felt that there was complex formation between the aniline and the HCl possibly as a simple Lewis acid adduct while Gerrard and Mooney (7) from their investigation of the structure of complexes of primary aromatic amines with boron trihalide proposed a structure of the hydrohalide of arylamine boron dihalide, FIGURE 10.

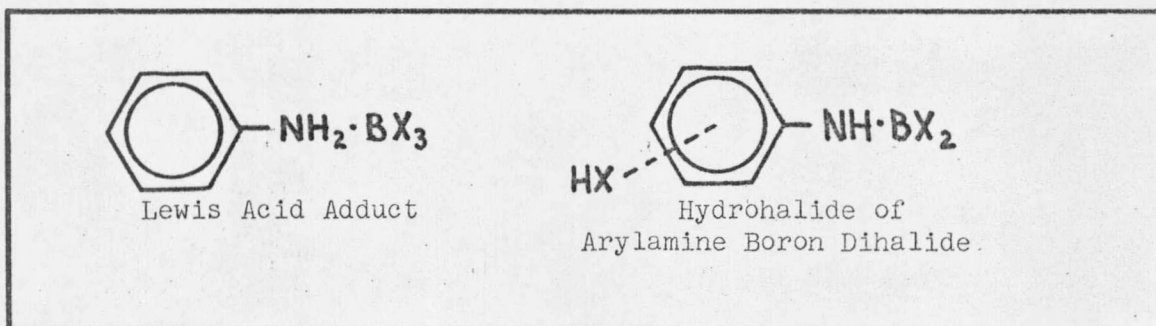


FIGURE 10: Possible Aniline-Halide Complex Structures

Attempts at identifying intermediates for the NiCl_2 system were unsuccessful, for while a dark viscous material could usually be isolated in the NH_4Cl condensation section of the reactor especially during low temperature or high space velocity runs, the separation and wet chemistry techniques subsequently applied to the material provided only inconclusive results indicating that some type of hydrochloride was present, but little more.

Considering the various factors previously discussed, that is, the interaction of the HCl with the catalyst, the adsorption of the nitrogen-

bearing compound, and the standard aromatic cracking mechanism, a plausible reaction sequence for the hydrodenitrogenation of indole is presented in FIGURE 11.

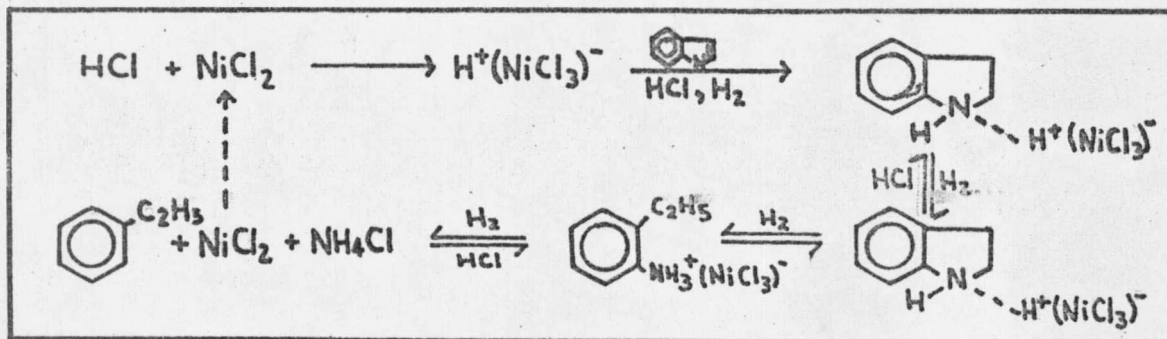


FIGURE 11: Possible Indole Hydrodenitrogenation Mechanism

Further speculation on feasible mechanisms would require a more intense study of the nature of the numerous possible intermediates and could best be accomplished through concentrating efforts on one or two nitrogen compounds (possibly a basic and a non-basic heterocycle) and applying more sophisticated techniques of identification.

V. SUMMARY AND CONCLUSIONS

The unusually high reactivity of the NiCl_2 -gaseous HCl catalyst system apparent for all compounds tested is probably due to the HCl atmosphere maintained over the catalyst. Not only does the HCl enhance the acidity of the alumina catalyst resulting in an interaction between the catalyst and the lone pair of electrons present on the nitrogen atom of the compound tested, but it also neutralizes the ammonia, the usual form of nitrogen leaving a denitrogenation system, to NH_4Cl , a solid. Basic compounds appear to be more readily removed than non-basic compounds probably the result of the acid-base interaction between catalyst and nitrogen compound, with this adsorption of the nitrogen compound onto the catalyst possibly being the rate controlling step in the reaction. However, the changes in reactivity with changing reactor temperature suggests that the mechanism of the hydodenitrogenation reaction may also be changing, perhaps so that C-N bond cleavage in the hydrogenated heterocyclic ring controls the reaction.

The over-all reaction probably follows the carbonium ion approach to cracking with the nitrogen compound adsorbed onto $\text{H}^+(\text{NiCl}_3)^-$ active sites. Hydrochloride intermediates are suspected in the reaction; however, no specific species were identified.

VI. RECOMMENDATIONS FOR FUTURE WORK

The most profitable course for future investigations of the NiCl_2 -gaseous HCl hydrodenitrogenation system would be to confine work to two typical heterocyclic nitrogen compounds, one basic and one non-basic. Positive identification of the intermediates should be made to determine the exact reaction sequence with gas chromatography, I.R. spectroscopy, mass spectroscopy or other instrumental techniques being more versatile than the wet chemistry approach.

The "reduced" conditions chosen for this work are too severe in that nitrogen removal was still at a very high level for all runs thereby decreasing the likelihood of isolating intermediates in the product. Some preliminary runs at low temperatures and pressures with a nitrogen compound such as quinoline which showed a high reactivity over the range of conditions employed here should be made to find conditions where nitrogen removal is less complete, perhaps only 50 or 60 percent effective.

VII. APPENDIX

TABLE 3: Properties of Commercial Catalyst (supplied by manufacturer)

Catalyst Manufacturer: The Harshaw Chemical Company

Identification Symbol: Al - 1602 - T

Properties: 1/8" silicated high activity alumina pellets

91% Al₂O₃ 6% SiO₂

Surface Area: 210 - 240 m²/g

Pore Volume: .48 cc/g^r

Apparent Bulk Density: 52 #/ft³

Average Pore Diameter: 91 - 80 Å

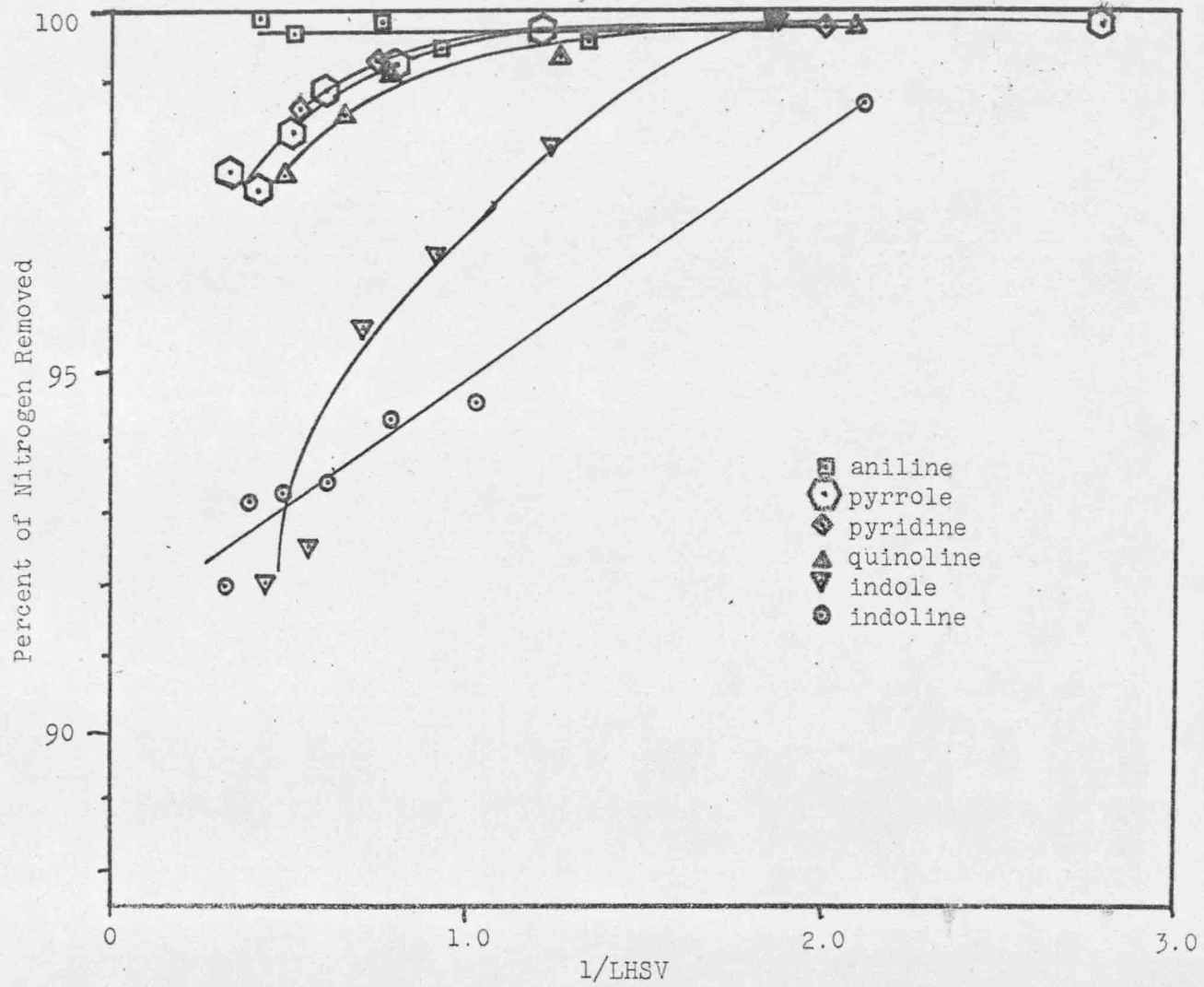


FIGURE 12: Test for Zero Order Kinetics

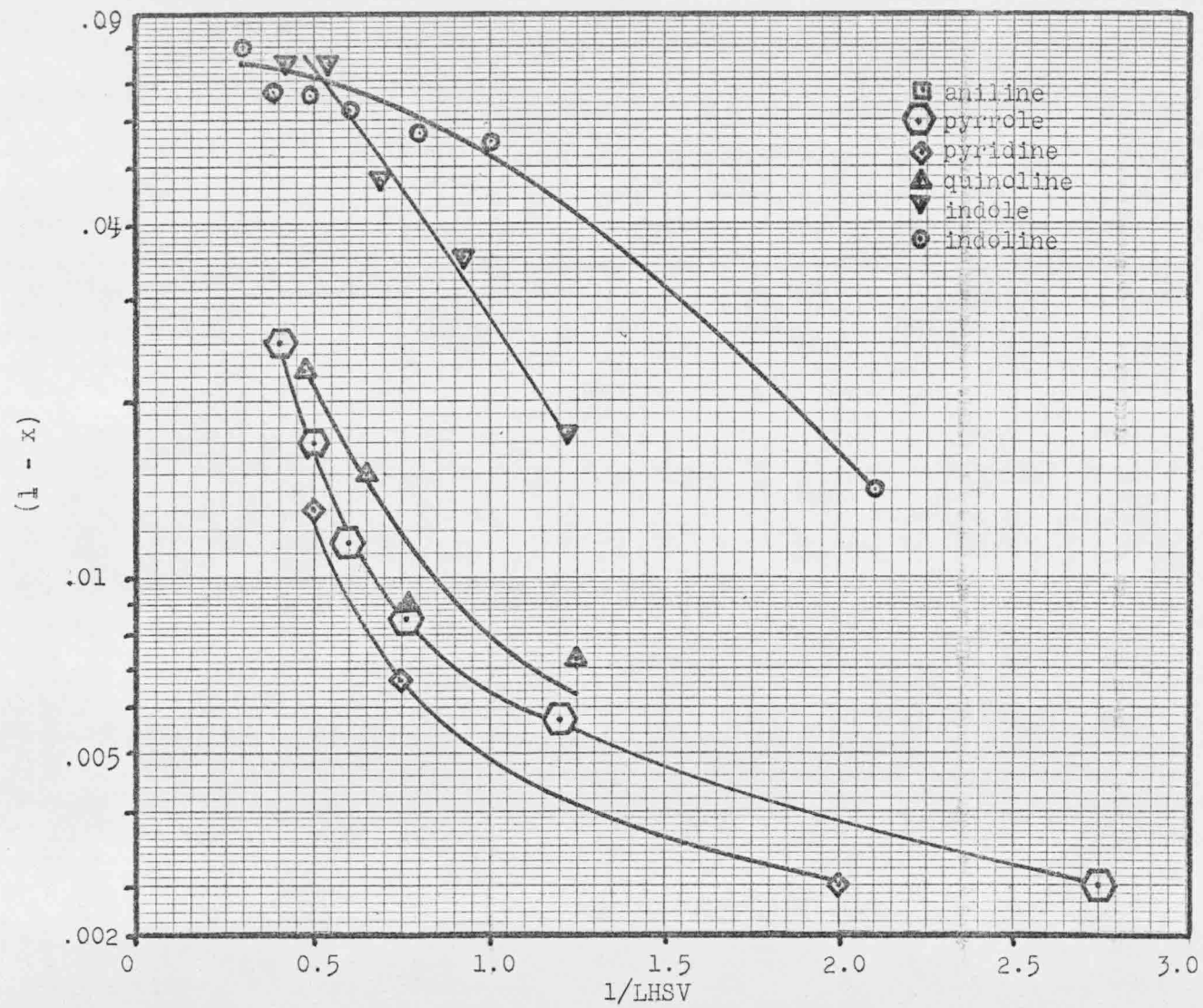


FIGURE 13: Test for First Order Kinetics

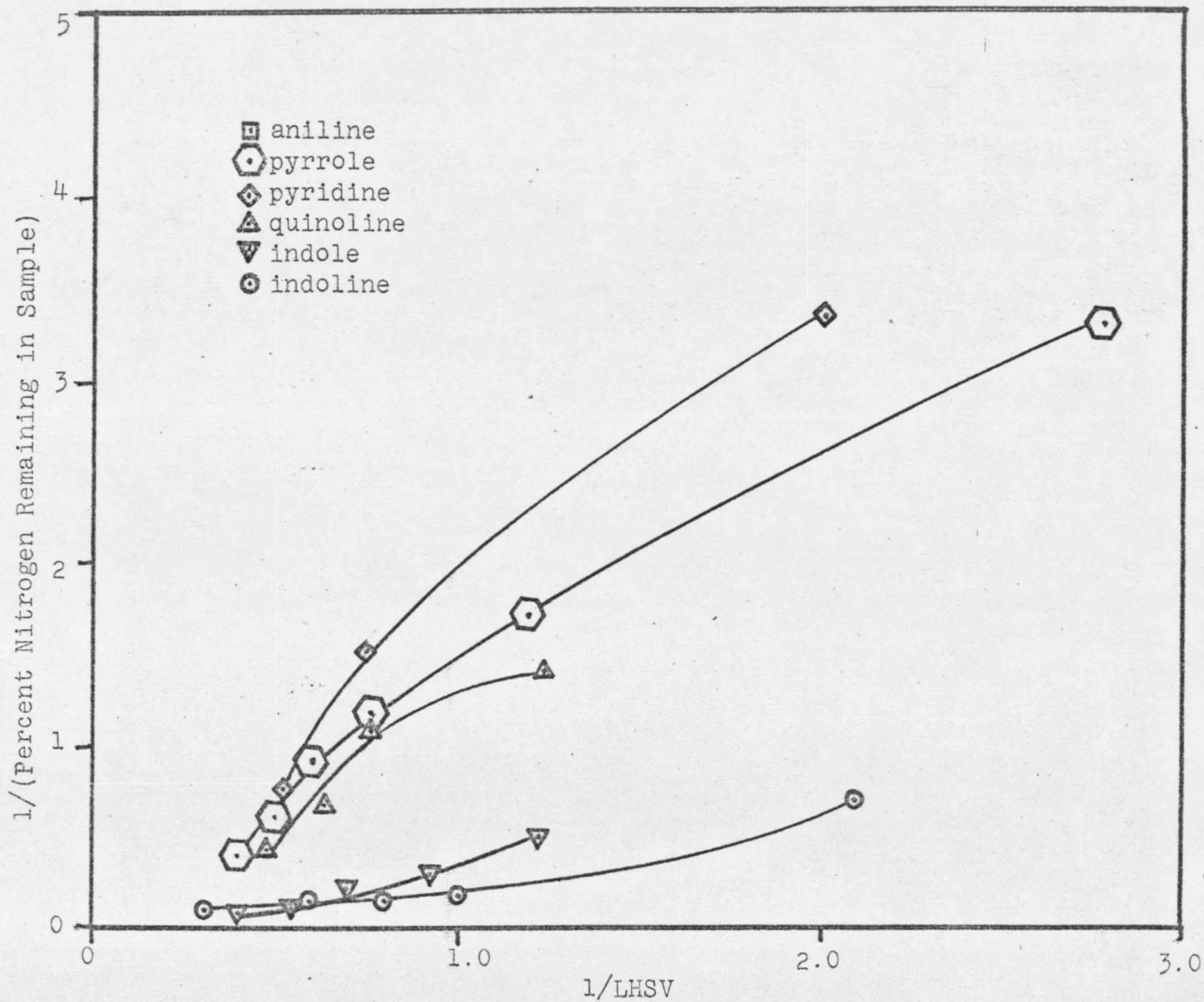
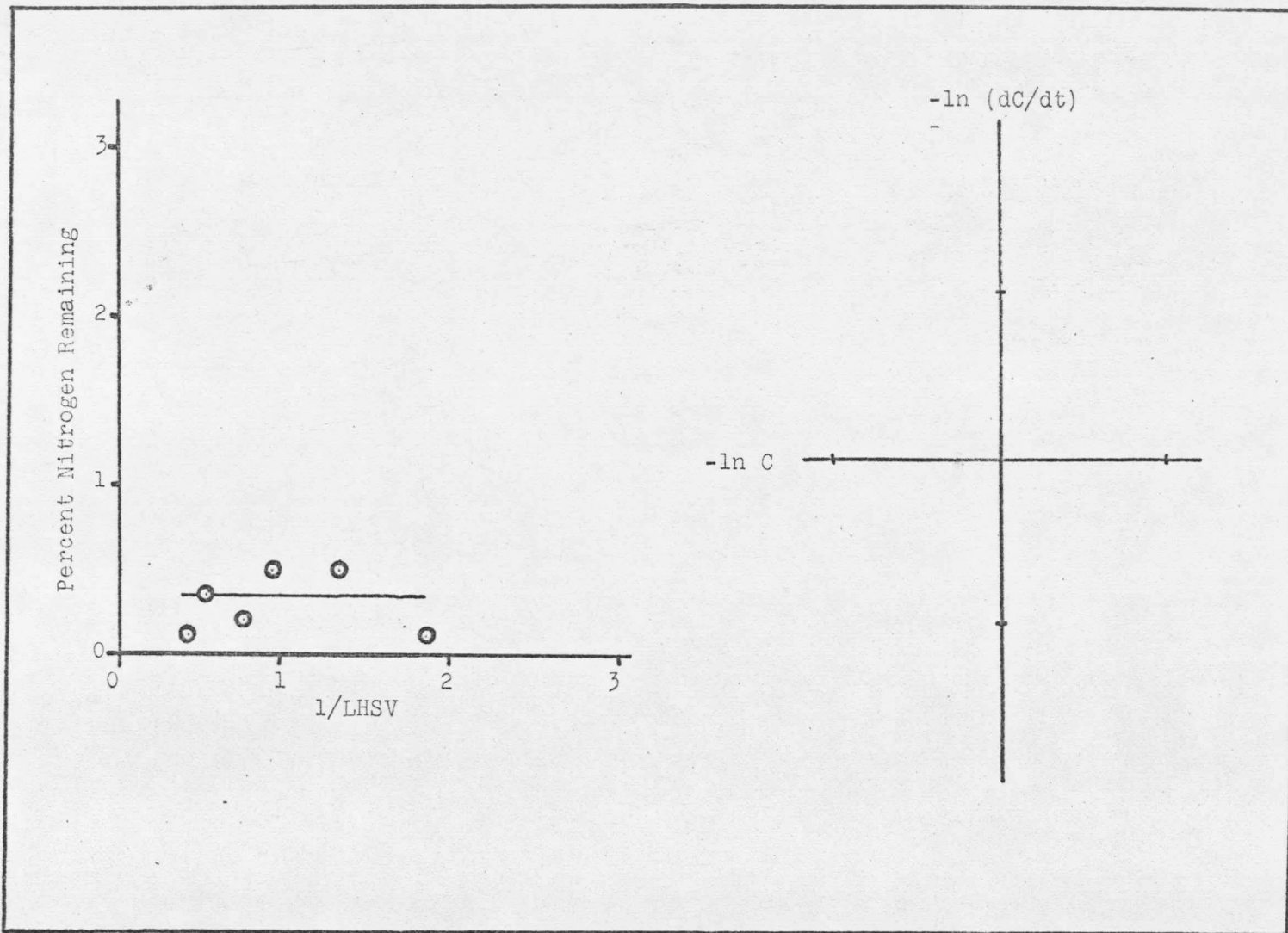


FIGURE 14: Test for Second Order Kinetics



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FIGURE 15: Differential Analysis of Aniline Data

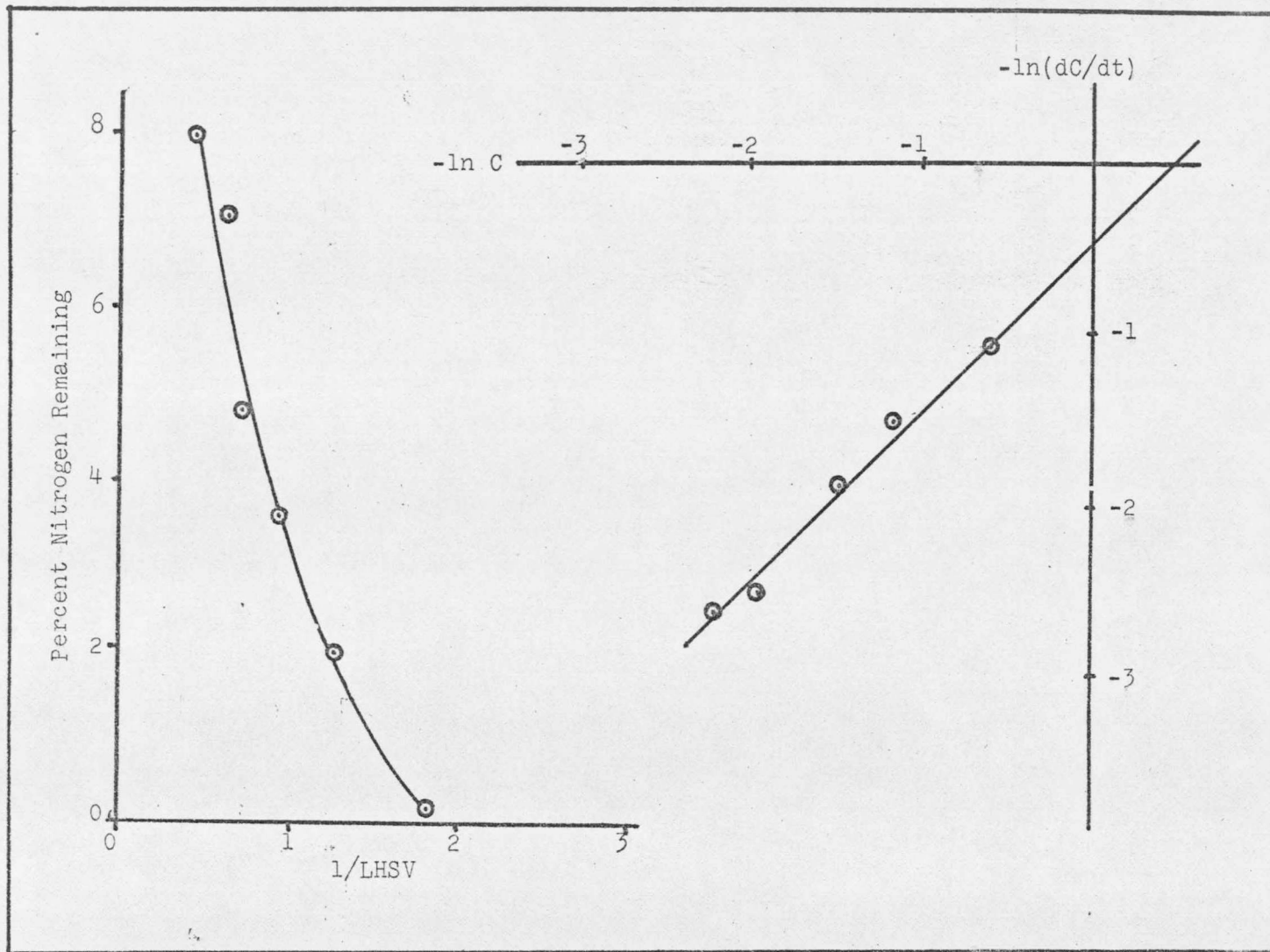


FIGURE 16: Differential Analysis of Indole LHSV Data

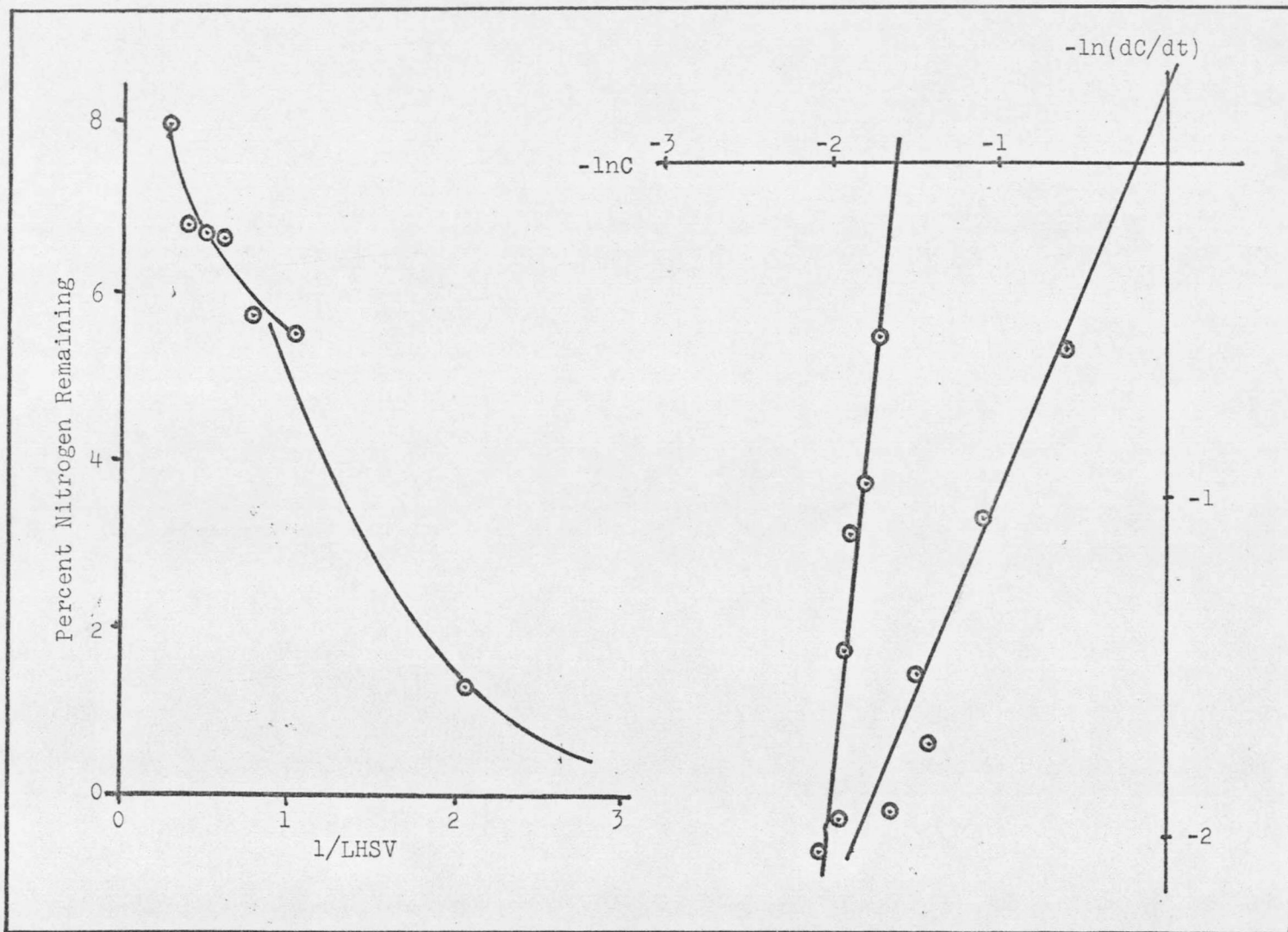


FIGURE 17: Differential Analysis of Indoline LHSV Data

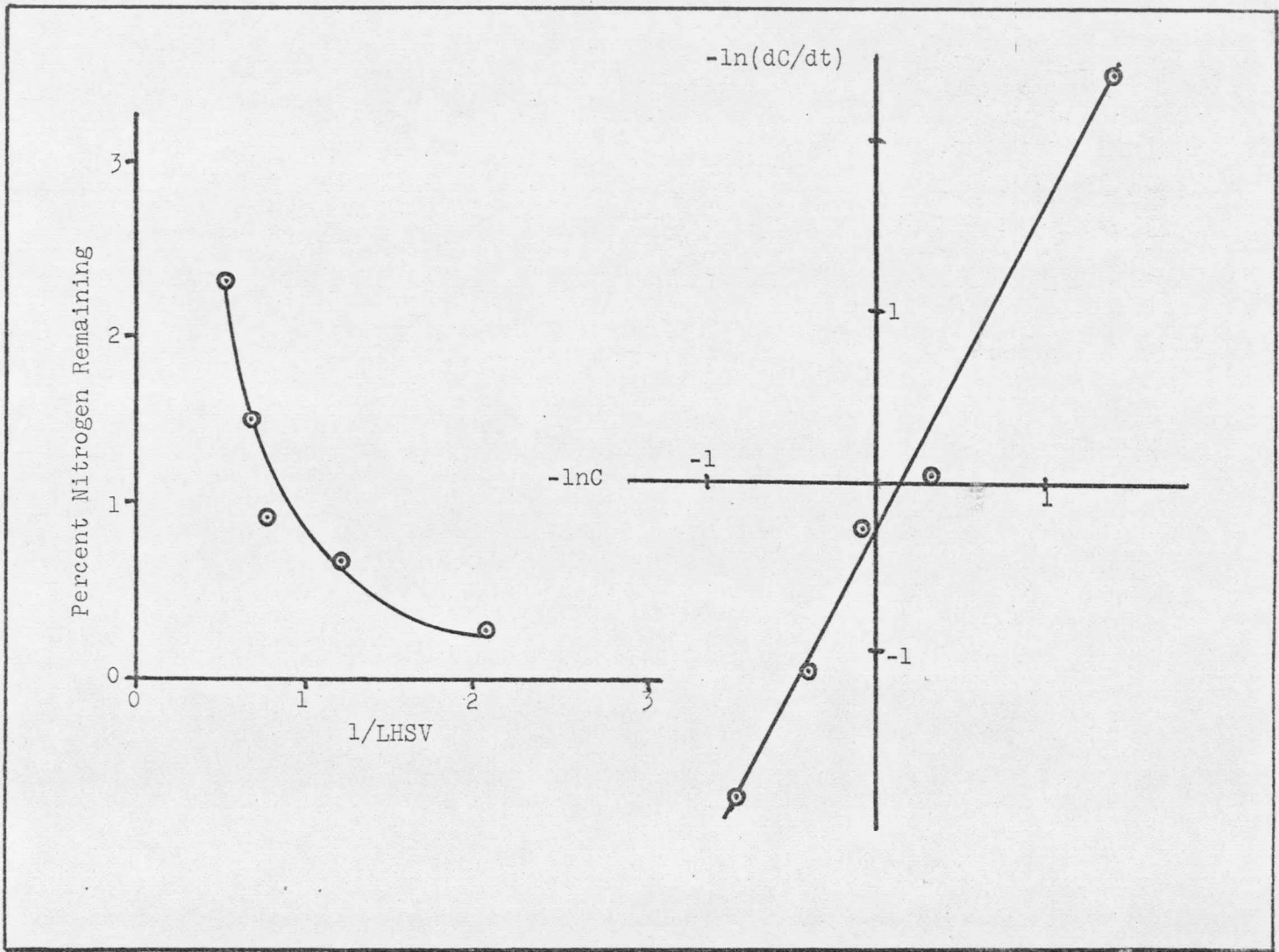


FIGURE 18: Differential Analysis of Quinoline LHSV Data

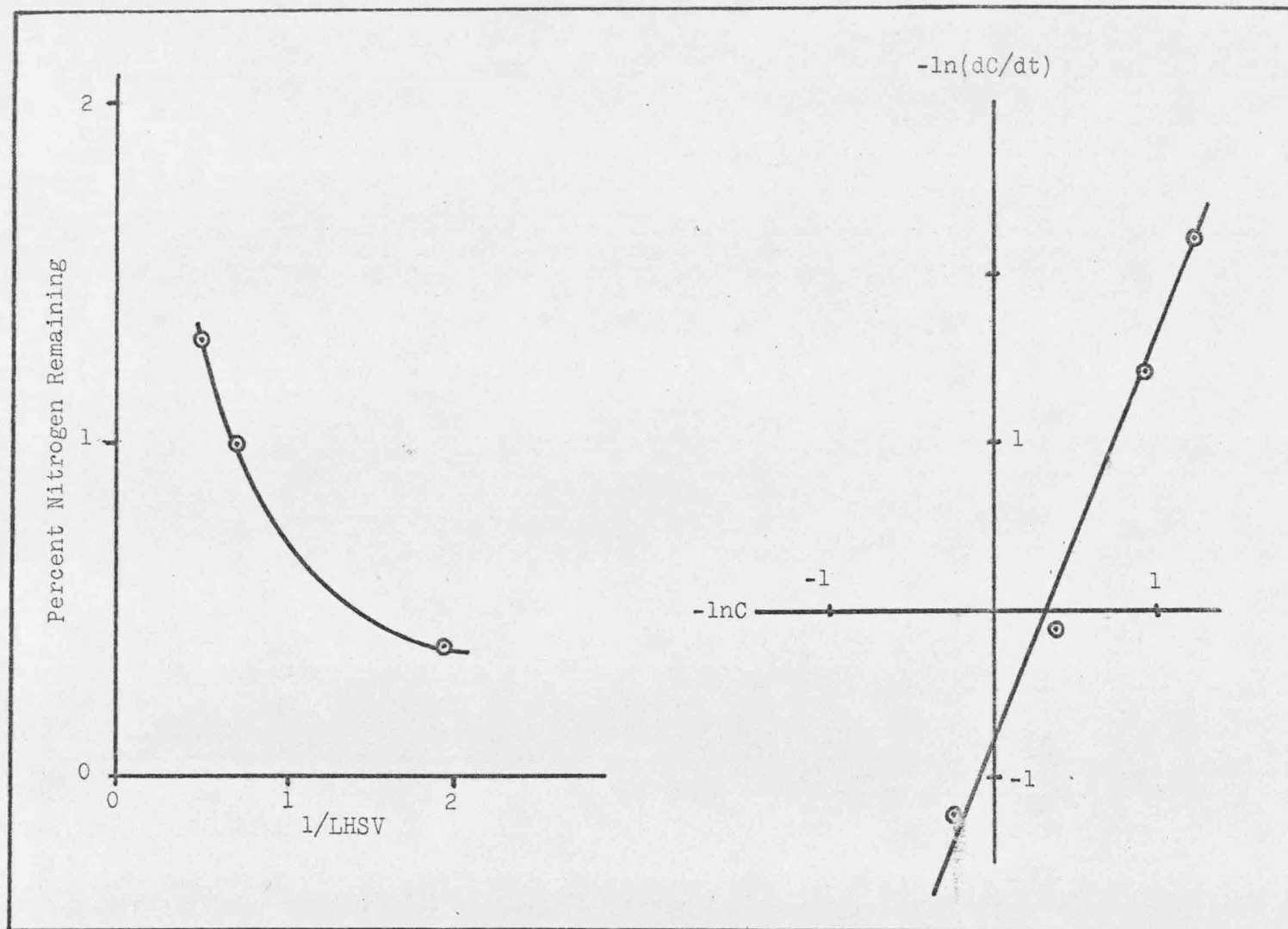


FIGURE 19: Differential Analysis of Pyridine LHSV Data

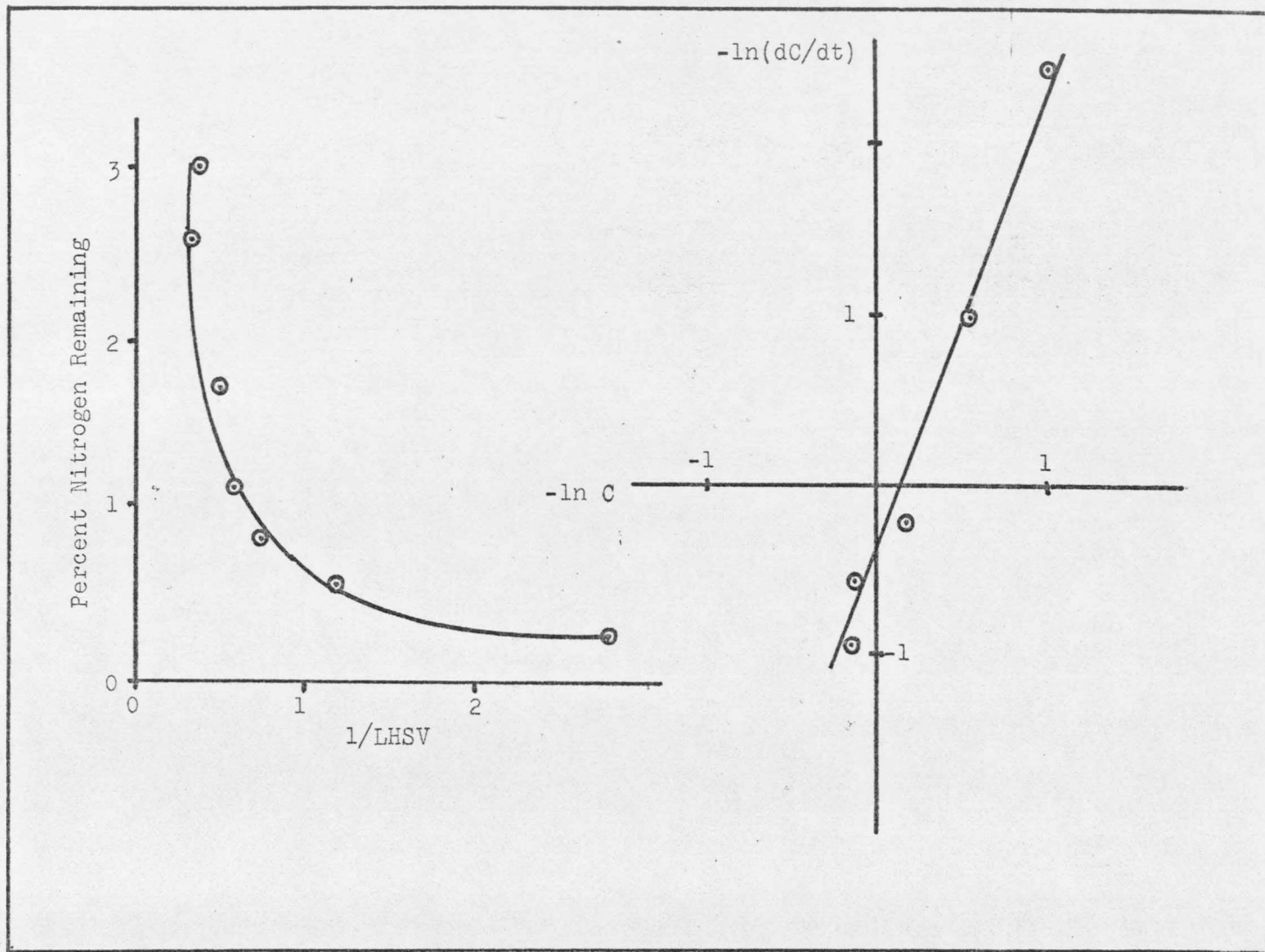


FIGURE 20: Differential Analysis of Pyrrole LHSV Data

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