Catalytic hydrodenitrogenation in the presence of chlorides
by Frank Philip McCandless

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 hydrodenitrogenation of a heavy California gas oil containing 0.515 percent nitrogen and 0.858 percent sulfur has been studied using a catalyst system consisting of alumina supported NiCl2 and HCl. The catalysts were made by impregnating a commercial alumina catalyst with aqueous solutions of the metal chlorides followed by drying at 230°C.

The nitrogen left the reaction zone combined in NH4C1.

The study was carried out in a fixed bed, tubular flow, integral reactor. The range of operating conditions was: Temperature 572 to 832°F. , Pressure 200 to 1200 psig, LHSV 1/8 to 2 cc oil/hr/cc catalyst, catalyst compositions 0 to 17.7 percent nickel and Cl to N ratios of 0 to 18.8 atom/atom. A hydrogen rate of 5000 SCF/bbl of oil was used for all tests. Methylene chloride, ethylene dichloride and gaseous HCl were investigated as a means of supplying HCl to the reaction zone. The chlorides decomposed to form HCl in the preheating section of the reactor.

At 800°F.,1000 psig, LHSV=1/2 and Cl/N=9.4, the nitrogen removal increased from 73.5 percent with no nickel on the alumina pellets to 92.5 percent with 4.2 percent nickel on the support. Increasing the nickel content above 4.2 percent to 17.7 percent increased the nitrogen removal to 94.2 percent. At 800°F, 1000 psig, LHSV=l/2 using a catalyst containing 6.1 percent nickel, the nitrogen removal was increased from 66 percent to 93 percent by increasing the C1/N ratio in the reactor from 0 to 18.8. However, at a Cl/N=9.4 conversion was about 90 percent. At 1000 psig, LHSV=l/2.and a Cl/N ratio of 9.4, the nitrogen removal . was increased from 54.5 to 92.5 percent by increasing the temperature from 572°F. to 832°F. Increasing reactor pressure from 200 to 1200 psig increased nitrogen removal from 62 to 93.5 percent at 800°F, LHSV=1/2 and Cl/N=9.4. At 800°F.,1000 psig, Cl/N=9.4, the reaction appeared to be 2nd order as shown by a plot of the concentration of nitrogen in the product as a function of space velocity.

At lower temperatures and pressures the mode of nitrogen removal was different. Under these conditions the nitrogen that was removed from the feed was combined in a heavy, viscous material that was insoluble in the product oil. This material was probably the hydrochloride of intermediate nitrogen bases formed in the reactor.

Sulfur removal followed the trend of nitrogen removal only at a lower level, At the optimum denitrogenation conditions sulfur removal was only 80,percent.

The catalyst system appeared to have considerable hydrocracking activity as shown by ASTM distillations of the product.

CoCl2 also showed a high denitrogenation activity while MnCl2 and SrCl2 were inactive.

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10988

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The hydrodenitrogenation of a heavy California gas oil containing 0.315 percent nitrogen and 0.858 percent sulfur has been studied using a catalyst system consisting of alumina supported $NiCl_2$ and HCl. The catalysts were made by impregnating a commercial alumina catalyst with aqueous solutions of the metal chlorides followed by drying at 230°C. The nitrogen left the reaction zone combined in NH_4Cl.

The study was carried out in a fixed bed, tubular flow, integral reactor. The range of operating conditions was: Temperature 572 to 832°F., Pressure 200 to 1200 psig, LHSV 1/8 to 2 cc oil/hr/cc catalyst, catalyst compositions 0 to 17.7 percent nickel and Cl to N ratios of 0 to 18.8 atom/atom. A hydrogen rate of 5000 SCF/bbl of oil was used for all tests. Methylene chloride, ethylene dichloride and gaseous HCl were investigated as a means of supplying HCl to the reaction zone. The chlorides decomposed to form HCl in the preheating section of the reactor.

At 800°F., 1000 psig, LHSV=1/2 and Cl/N=9.4, the nitrogen removal increased from 73.5 percent with no nickel on the alumina pellets to 92.5 percent with 4.2 percent nickel on the support. Increasing the nickel content above 4.2 percent to 17.7 percent increased the nitrogen removal to 94.2 percent. At 800°F, 1000 psig, LHSV=1/2 using a catalyst containing 6.1 percent nickel, the nitrogen removal was increased from 66 percent to 93 percent by increasing the Cl/N ratio in the reactor from 0 to 18.8. However, at a Cl/N=9.4 conversion was about 90 percent. At 1000 psig, LHSV=1/2 and a Cl/N ratio of 9.4, the nitrogen removal was increased from 54.5 to 92.5 percent by increasing the temperature from 572°F. to 832°F. Increasing reactor pressure from 200 to 1200 psig increased nitrogen removal from 62 to 93.5 percent at 800°F, LHSV=1/2 and Cl/N=9.4. At 800°F., 1000 psig, Cl/N=9.4, the reaction appeared to be 2nd order as shown by a plot of the concentration of nitrogen in the product as a function of space velocity.

At lower temperatures and pressures the mode of nitrogen removal was different. Under these conditions the nitrogen that was removed from the feed was combined in a heavy, viscous material that was insoluble in the product oil. This material was probably the hydrochloride of intermediate nitrogen bases formed in the reactor.

Sulfur removal followed the trend of nitrogen removal only at a lower level. At the optimum denitrogenation conditions sulfur removal was only 80 percent.

The catalyst system appeared to have considerable hydrocracking activity as shown by ASTM distillations of the product.

$CoCl_2$ also showed a high denitrogenation activity while $MnCl_2$ and $SrCl_2$ were inactive.

I. INTRODUCTION

A. Background

The removal of nitrogen from petroleum oils is a very important operation in petroleum refining because many of the difficulties of processing and of preparing acceptable products can be traced directly to the nitrogen containing compounds present in the oil. Nitrogen removal will become even more important in the future because of the depletion of high quality nitrogen free crude oils and with the use of shale oils which contain a very high percentage of nitrogen compounds.

In the problems of processing, nitrogen compounds are severe catalyst poisons and hence feed streams to most catalytic processes must be essentially free from nitrogen compounds if optimum conversion of the feed stocks is to be obtained. The nitrogen compounds being basic in character react or otherwise interact with acid functions of the catalysts to reduce activity. For example, nitrogen containing compounds have been shown to be severe poisons for acid alkylation, polymerization, isomerization, catalytic cracking and hydrocracking catalysts.[14,20,22] This poisoning can best be illustrated by a specific example such as the data reported by Jacobson which shows the effect that nitrogen compounds have on the hydrocracking of a light cycle oil in the presence of a cobalt sulfide catalyst.[14] These data are shown in the table below:

TABLE I

Example of Nitrogen Poisoning

Nitrogen content of feed stream	Time conversion can be maintained at 60% per pass before raising reactor temperature to 715° F.
0.1 PPM	4,000 hours
1.5 PPM	2,500
100 PPM	<100

Obviously a very low concentration of nitrogen in the feed stream is required if the hydrocracking process is to be feasible. There are many similar studies reported in the literature which show the adverse effect that nitrogen compounds have on catalytic activity.

In petroleum products, nitrogen compounds adversely affect product color, stability[28], odor, and some nitrogen compounds have been shown to suppress detonation and tetraethyl lead response[15]. Nitrogen compounds are also involved in the formation of gums[16,28] and sludges in petroleum products.

Obviously then, there is adequate justification for the treating of many feed stocks and products for nitrogen removal.

B. Methods of Denitrogenation

Many of the basic nitrogen compounds can be removed from petroleum oils by extraction with a dilute solution of a strong mineral acid[18]. However, this is a very inefficient method and complete denitrogenation is not possible since, in general, less than half of the nitrogen

compounds found in petroleum oils are basic[23,24]. Also, in extraction process the whole nitrogen containing molecule is removed. In the heavier oils this can amount to a large loss in product since, even though the nitrogen content of the oil may be less than 1%, the nitrogen compound content may run as high as 10 to 20 percent by weight [15].

Adsorption methods can also be used to remove nitrogen compounds from oils and in this case the removal is nearly complete[26]. However, this method still has the disadvantage of having a high loss in raw materials since, again, the whole nitrogen containing molecule is removed. Because of the limitations of the physical methods mentioned above, hydrogenation has become a popular method of denitrogenating petroleum oils. It has the advantage that it is selective because it removes only the nitrogen atom from the heterocyclic molecule and the remaining product is a usable hydrocarbon. It also has a processing advantage because the hydrodenitrogenation process is continuous while adsorption requires a cyclic operation.

Hydrogenation is a very effective method for removing the nitrogen from light petroleum oils, however, extreme conditions of temperature and pressure are required to denitrogenate heavy gas oils using present catalysts.[10,14] For example, Flinn and co-workers showed that a heavy naphtha containing only 240 PPM nitrogen can be easily freed of nitrogen by hydrogenation in the presence of an active nickel tungsten

sulfide catalyst at 300 psig, 600°F. and a 4.0 LHSV (liquid hourly space velocity cc oil/hr/cc catalyst). However, if the feed is a deasphalted residuum containing 2800 PPM nitrogen the product from hydrodenitrogenation at 6000 psig, 740°F., and a 0.5 LHSV still contained 250 PPM nitrogen.[10] This level of nitrogen is still too high for the feed to most catalytic operations.

A more active catalyst would significantly reduce the temperature and pressure needed for hydrodenitrogenation and permit the optimum use of heavy oils which contain a high level of nitrogen. For this reason a catalyst has been sought which is more active than the commercial hydrodenitrogenation catalysts presently available.

C. Types of Nitrogen Compounds in Petroleum

Nitrogen compounds present in petroleum have been studied extensively since the importance of these compounds toward catalytic behavior has been recognized.[1,3,10,18,23,24,26] The amount of nitrogen present in petroleum varies widely with crude source. Perhaps the extremes of American crudes can be shown by comparison of Ponca City (Oklahoma) and Wilmington (California) crudes.[3] The amount of nitrogen present in these crudes is shown below in Table 2 together with the composition of another California oil to show that nitrogen content varies considerably within a given district.

TABLE II

Analyses of Crude Petroleum for Sulfur and Nitrogen

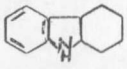
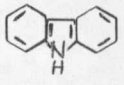
Wt. %	Ponca City (Okla.)	Wilmington (Calif.)	Midway (Calif.)
Sulfur	0.11	1.53	0.94
Nitrogen	0.01	0.65	0.41

These compare with a national average of about 0.15 percent nitrogen.

In general, less than 50 percent of the nitrogen compounds found in petroleum are basic.[23,24] Typical basic compounds are alkylated pyridines, quinolines, benzoquinolines, indolines, hydrocarbazoles and amines while typical non-basic compounds are alkylated pyrroles, indoles and carbazoles.[1,3,10,23] The structure of these compounds is shown in Table 3.

TABLE III

Typical Nitrogen Compounds Found in Petroleum

Basic Compounds		Non-Basic Compounds	
	Quinoline		
	Pyridine		Pyrrole
	Indoline		Indole
	Hydrocarbazole		Carbazole
$R\text{-}NH_2$	Amine		

It has been found that the amines and 5-membered ring compounds are fairly easy to denitrogenate while the aromatic stabilized ring

types are harder to denitrogenate. Pure component studies have shown that the rate of removal of nitrogen from amines is about 10 times that of quinoline while indole had a rate of removal of about 4 times that of quinoline at the same conditions. The nitrogen compounds found in the higher boiling petroleum fractions are much harder to denitrogenate, possibly because of steric hindrance due to the presence of large groups attached to the nitrogen containing ring[10].

D. Hydrodenitrogenation Catalysts

At the present time catalysts developed for desulfurization are used for denitrogenation also. The most effective catalysts appear to be sulfided cobalt or nickel molybdate on alumina or silica alumina.[6] These catalysts contain from 2 to 6 percent NiO or CoO together with 15 to 16 percent MoO_3. However, Jacobson has shown that increased denitrogenation activity results when the metal content is increased above 20 percent in making a nickel molybdate hydrodenitrogenation catalyst.[14] Falk compared the denitrogenation activity of nine commercial nickel molybdate and cobalt molybdate hydrotreating catalysts and found that activity varied widely even though the catalyst compositions were essentially identical. For example, two catalysts, both containing 3.0% CoO and 15.0% MoO_3, gave nitrogen removal of 85.0% and 50.0% during tests using the same oil and identical operating conditions.[9]

Other catalysts are also used for hydrodenitrogenation. Flinn and co-workers used an extremely active nickel tungsten sulfide catalyst for extensive hydrodenitrogenation studies.[10] Falk studied nickel tungsten sulfide as a catalyst in the hydrodenitrogenation of a heavy California gas oil and concluded that the activity did not vary greatly with metal content and catalyst composition.[9] There are many more examples in the literature of the use of these and other metals as hydrodenitrogenation catalysts.

E. The Mechanism of Hydrodenitrogenation

Mechanism studies of the hydrodenitrogenation reaction in the presence of a cobalt molybdate catalyst indicate that the following mechanism is probable in the destructive hydrogenation of quinoline at 830°F. and 500 psig:[8]

(1) The nitrogen compound is adsorbed on an "active site" of the catalyst where the chemisorbed compound reacts with absorbed molecular hydrogen to form hydrogenated intermediates. The final intermediate is an amine which results from ring cleavage.

(2) The chemisorbed amine or aminium ion exerts a strong inductive effect of electron attraction which renders the nitrogen-carbon bond susceptable to the electrophilic attack of hydrogen. The products of this step are absorbed ammonia and a hydrocarbon.

(3) The products are then desorbed.

The last reaction step is a simple hydrocracking reaction.[10] Some other important indications are that:

(1) Chemisorption of nitrogen compounds is effected by the interaction of the basic function of the nitrogen compound and acidic functions of the catalyst.

(2) The chemisorption preference of the catalyst toward different nitrogen containing compounds is proportional to the basic strength of the nitrogen compound.

(3) This chemisorption preference of the acid site is such that the catalyst is poisoned for the reaction of less basic compounds, by compounds of higher basic strength.

This work also showed that at 830°F. the adsorption of quinoline was the rate controlling step although work by another worker at 725-750°F. showed that one of the surface reactions controlled the overall rate at the lower temperature[25].

In these studies the active principle of the catalyst was identified as being that of an "acid" and a single site mechanism was pictured.

More recently, however, the sulfide catalysts used in hydrodenitrogenation have been identified as "dual-functional".[29,30] These catalysts have been shown to contain geometrically separate catalyst components which catalyze different steps in the overall reaction. In

fact, recent work has shown that the catalyst components can be separated by macroscopic distances and still function properly.[30] Thus hydrodenitrogenation catalysts can function simultaneously as hydrogenation, splitting or cracking, and to some extent isomerization catalysts and probably at various stages in the overall reaction, intermediates must migrate between "metal" and "acidic" components of the dual functional catalysts.

Mechanism studies using dual functional catalysts as hydrocracking catalysts have shown that, among other roles, the main function of the metal component is one of hydrogenation and dehydrogenation while that of the acidic component is cracking. This is also probably true in hydrodenitrogenation. Thus the hydrogenation of the nitrogen compound probably takes place on the metal sites and the intermediates must then migrate to acid sites where the final hydrocracking reaction takes place. In fact, increased hydrogenation activity appears to be the main purpose of iron, cobalt or nickel "promoters" in hydrodenitrogenation catalysts.[14] It has also been shown that increased activity results when a silica alumina "acidic" support is used in making hydrodenitrogenation catalysts.

As a general rule the overall rate of reaction is controlled by the reactions taking place on the acidic sites[31] and activity of these catalysts usually declines with time because of the gradual coking of the acidic sites.[4]

Thus, the framework of the reaction mechanism for hydrodenitrogenation is probably about as pictured above, except that hydrogenation and cracking reactions probably take place on different sites of the catalyst and that intermediates must migrate between sites during the course of the reaction.

Naturally, the rate controlling step could be any one of the adsorption, desorption, or migration steps or, a "surface reaction" could control depending upon reactor conditions.

II. HYDRODENITROGENATION IN THE PRESENCE OF CHLORIDES

A. Introduction

Hydrodenitrogenation studies have been going on at Montana State University for sometime. During some exploratory hydrodenitrogenation catalyst tests a high removal of nitrogen from a test oil was observed when metal chlorides were used as intermediates in making manganese sulfide catalysts. Nitrogen left the reaction zone in the form of NH_4Cl indicating that chloride catalysts may be a means of substantially removing nitrogen from petroleum oils. Since present commercial catalysts are less active than the initial activity shown by the manganese chloride catalysts, the use of chlorides as hydrodenitrogenation catalysts was investigated further.

Initial data showed that the chloride catalysts deactivated rapidly, presumably with the removal of chlorine from the reaction zone as ammonium chloride, however, subsequent runs showed that activity of the manganese chloride catalyst could be maintained for a time by continuously adding an organic chlorine compound to the reaction zone. Apparently the chlorine compound was converted to a hydrocarbon and HCl in the reactor preheating zone. The preliminary data are shown in Figure 1 which shows the nitrogen removed from the test oil as a function of time for various manganese chloride catalysts and different space velocities. These tests were run at 800° F., 1000 psig, with a hydrogen rate of 5,000 SCF/bbl. As can be seen from this figure, the nitrogen removal was increased by increasing the

manganese chloride content of the catalyst and by decreasing the space velocity. Finally the activity was increased and maintained for a 10 hour period at about 90 percent by continuously adding methylene chloride to the reactor with the feed. For these preliminary test runs a 10 hour run was about the maximum length that could be made due to the accumulation of NH_4Cl at the outlet which eventually plugged up the reactor.

Based on these preliminary data a new reactor was built so that the use of metal chlorides as hydrodenitrogenation catalysts could be thoroughly studied. The new reactor was designed so that a several day accumulation of NH_4Cl could be tolerated and long test runs could be made.

B. Experimental

(1) Reactor

As mentioned above, the preliminary test data showed that the nitrogen from the hydrodenitrogenation reaction left the reactor in the form of ammonium chloride, NH_4Cl. This material is a dissociated gas at the reaction temperature of 800°F. but is a solid at the cool reactor outlet (sublimation temperature = 635°F.[12]). The accumulation of this material quickly plugged up the reactor outlet of the existing test reactor. For this reason it was necessary to design a special reactor so that a build up of the solid NH_4Cl could be tolerated over a long period of time. At the same time, inspection

of the old stainless steel reactor showed that a considerable amount of corrosion was taking place in its interior. To eliminate most of the corrosion problem the new reactor was constructed of Inconel alloy. This alloy, which contains about 72 percent nickel, 15 percent chromium and about 13 percent iron, is said by the manufacturer to have the highest permissible operating temperature in hydrogen chloride of any of the common alloys.[13] A sketch of the Inconel reactor is shown in Figure 2. It was constructed of a 53 inch length of schedule 80 1-inch Inconel alloy 600 pipe. A high pressure stainless steel head was threaded to the alloy pipe at the upper end of the reactor. This head had connections for the feed nozzle, a rupture disc and for the thermowell. A monel screen was placed over the extreme reactor outlet to keep NH_4Cl and other solid particles from reaching the pressure control valve. During operation the reactor tube was mounted in a 6 inch diameter solid aluminum block 30 inches long. Three 13 ohm nichrome heating coils strung on ceramic beads were wound on grooves in the aluminum block. These heating coils were independently controlled by separate variacs. The block-heater assembly was permanently mounted in an outer metal shell 12 inches in diameter which was filled with "Zonolite" insulating material. A thermowell was mounted axially in the reactor and secured to the reactor head by means of a special fitting. It was constructed of a 1/4" x 0.05" wall Inconel tube welded shut at one end. Four iron-constantan thermocouples were inserted in the

thermowell, one each at the top, middle and bottom of the catalyst zone and one at the extreme reactor outlet. These thermocouples were connected to a Leeds and Northrup indicating potentiometer. The bottom part of the reactor, which protruded down from the aluminum heating block, was used as a precooling section. Ammonium chloride was deposited in this section as it left the reaction zone. A movable heater was mounted on this section of pipe and was used intermittently to obtain an even distribution of the solid ammonium chloride as it was deposited.

A sketch of the entire reactor system is shown in Figure 3. During operation the oil was fed from the oil reservoir by means of a "Lapp Pulsa-Feeder" pump. The oil rate was measured by means of a small burette attached to the feed system. High pressure electrolytic hydrogen was obtained in bottles, the pressure reduced through a pressure regulator and the flow rate measured by means of a high pressure rotometer. The reactor pressure was controlled by means of a diaphragm type back pressure regulator.

(2) Reactor Preparation and Operation

In preparing for a run, the reactor was loaded with catalyst, purged with hydrogen to remove air, pressurized and tested for leaks before heating to reaction temperature. In all cases a catalyst charge of 120 cc was used. The catalyst bed was held in place top and bottom with approximately 90 cc of 1/4 inch alundum pellets. This centered

the catalyst bed in the middle of the heater block. The whole catalyst-support bed was held in the upper part of the reactor by means of a nickel-iron wire ring. After purging and pressure testing, the reactor was allowed to heat overnight in preparation for the run. When the reactor had reached a temperature approximately 100° C. below the desired operating temperature, oil and hydrogen was fed to the reactor and the pressure increased to the desired operating pressure. The temperature was then brought rapidly to the desired operating temperature. The desired oil flow rate was obtained by measuring the volumetric rate of flow from the burette. The flow rates and temperatures were recorded periodically and adjustments made when required.

(3) Catalyst Preparation

Except for the few catalysts made for the preliminary test runs, all catalysts were made using the same alumina support. This alumina (Harshaw AL-1802-E) had proved to be the best support for a nickel-tungsten sulfide hydrodenitrogenation catalyst[9] and preliminary runs had showed that a slightly greater activity was obtained when the Harshaw alumina was used in making manganese chloride catalysts. The physical and chemical properties of this material are shown in Table 4.

In making the catalyst, the alumina pellets were first dried for about 24 hours at 230° C. The dry pellets were then impregnated

with an aqueous solution of the metal chloride by adding the alumina pellets to the solution and letting them set approximately 24 hours. The excess solution was drained from the pellets and they were dried in an oven for about two days at 230° C. The catalyst pellets were not treated further after drying.

(4) Test Oil Properties

Two barrel samples of a high nitrogen content California gas oil were obtained from the Chevron Research Company and used for the catalyst tests. The oil was designated by the company as Midway gas oil and contained about 3100 PPM nitrogen. Physical and chemical properties of the two barrel samples are shown in Table 5.

(5) Analytical Methods

All oil samples were analyzed for total nitrogen content by a modified Kjeldahl method.[17] Sulfur and chlorine analyses were made using the quartz tube combustion method for testing for sulfur in petroleum oils.[2]

C. Comparison of Various Metal Chlorides as Hydrodenitrogenation Catalysts

Several metal chloride catalysts were made as described above and tested as hydrodenitrogenation catalysts at 1000 psig, 800°F, using a LHSV (liquid hourly space velocity) of 1/4 and a hydrogen rate of 5000 SCF/bbl of oil. This hydrogen rate was used throughout this work. It was chosen based on the work of Falk[9], who showed

that below a hydrogen rate of about 4,000 SCF/bbl nitrogen removal was affected by changes in hydrogen rate, while above this rate, nitrogen removal was constant. In other words, film diffusion was not controlling at this hydrogen rate. Chlorine was continuously added to the reaction zone with the feed in the form of methylene chloride sufficient to give a Cl/N ratio of 9.4 $^{atom}/_{atom}$ (5% CH_2Cl_2 based on feed volume). Apparently the methylene chloride was converted to HCl in the reactor preheating section. This amount of chloride was chosen arbitrarily for the first tests.

The results of these tests are shown in Figure 4. As can be seen from the figure, cobalt and nickel chloride gave excellent nitrogen removal leveling off at about 97 and 95 percent respectively while strontium chloride showed very little catalytic activity, removing only about 75 percent of the nitrogen. Activity started off at a high level, removing over 90 percent of the nitrogen, when manganese chloride was tested but decreased rapidly to a point where only about 70 percent was removed. Since an extensive survey of the use of other metals as catalysts was not desired at this time, and since excellent nitrogen removal was obtained using the nickel chloride-HCl system and cobalt chloride-HCl system, it was decided to limit subsequent tests to either nickel or cobalt.

The chlorides of cobalt and nickel exert a considerable vapor pressure at higher temperatures and it would be conceivable that the

metal catalyst could be lost from the support because of this. In comparing the vapor pressures of the two metal chlorides it is found that above about 925° C, the vapor pressure of nickel chloride is much higher than that of cobalt chloride, however at the temperatures of interest for the hydrodenitrogenation reaction the vapor pressure of $NiCl_2$ is lower than that of $CoCl_2$. This is shown in Figure 5 which shows the logarithm of the vapor pressure of the two metal chlorides as a function of reciprocal temperature. For this reason it was decided to make a thorough study of the supported $NiCl_2$-HCl system rather than $CoCl_2$ as a hydrodenitrogenation catalyst.

D. Effect of Catalyst Composition

Tests were made of catalysts containing various amounts of nickel chloride to determine the optimum catalyst composition with respect to denitrogenation. The results of these tests are shown in Figure 6 which show the percentage of nitrogen removed as a function of catalyst composition. In all cases the nitrogen removed is based on samples taken after approximately 48 hours on stream, a time sufficient for the catalyst to "line out". The nitrogen removed as a function of time for the various catalysts is shown in Figure 7 to show the line out time. For these runs reactor conditions of 800° F., 1000 psig, LHSV= 1/2 and 5000 SCF H_2/bbl of oil were used. Again a Cl/N ratio of 9.4 was maintained with methylene chloride since this had proved to be satisfactory in the first trials.

As can be seen from Figure 6, a small amount of metal increased the activity appreciably. Nitrogen removal increased from about 73 percent to 85 percent by adding 0.1% nickel however, the incremental increase in activity was less when the nickel chloride content was increased above this trace amount. Increasing the metal content above about 4 percent did not significantly increase the nitrogen removal above about 92 percent.

E. Comparison of Activity of $NiCl_2$ and NiO catalyst

A catalyst was made by impregnating the alumina pellets with a solution of nickel nitrate followed by drying and calcination in air at 900° F. thus converting the nickel nitrate to NiO. The finished catalyst contained 4.7 percent nickel. This catalyst was tested at 800° F, 1,000 psig, LHSV= 1/2 and Cl/N= 9.4 for comparison with the catalyst used in the previous test which contained 4.1 percent nickel, impregnated as the chloride. The results of the two test runs are shown in Figure 8 which shows the nitrogen removal as a function of time. As can be seen from the figure, the nickel chloride catalyst is somewhat more active than the nickel oxide catalyst, removing about 92 percent of the nitrogen compared with about 85 percent with the NiO.

So that all reactor and feed variables could be studied on the same basis, a large batch of catalyst was made and used for all subsequent runs. The catalyst contained 6.1% nickel impregnated

on the same carrier, AL-1802-E alumina.

F. Effect of Type of Chloride Fed on Catalyst Activity

In the first test runs chloride, as methylene chloride, was fed to the reaction zone along with the oil simply because it worked; that is, activity was maintained at a high level when methylene chloride was added with the feed. The off gas from the product smelled strongly of HCl indicating that this was the species that maintained activity. To test this, runs were also made using ethylene dichloride and gaseous HCl. For the HCl run the gas was mixed with the hydrogen feed to give the desired Cl/N ratio. For these runs the 6.1% nickel catalyst was used while other reactor conditions were held at 800° F., 1000 psig and LHSV=1/2. The results of these test runs are shown in Figure 9 together with the results of a run using methylene chloride. As can be seen from the figure, there appears to be no significant difference in the nitrogen removal between the three runs using the three compounds as a means of adding chloride. In all three runs the nitrogen removal was about 90 percent. In all subsequent runs methylene chloride was used as a means of supplying chloride because a supply of it was readily available.

G. Effect of Cl/N Ratio on Nitrogen Removal

Test runs were made using the 6.1% Ni catalyst and Cl/N ratios of 0, 1.88, 4.70, 9.40 and 18.80 to determine the effect of this

variable on nitrogen removal. Other reactor conditions were 800° F., 1000 psig and LHSV=1/2. Methylene chloride was used to supply the chloride. The results of these tests are shown graphically in Figure 10 which shows the nitrogen removed as a function of Cl/N ratio. Increasing the Cl/N ratio up to a point increased hydrodenitrogenation activity however, an increase well above the stoichiometric ratio required for combination with each nitrogen atom was required to maintain the activity at a high level. With no chloride in the feed, about 67 percent of the nitrogen was removed, and increasing the Cl/N ratio up to 9.4 increased the removal to about 90 percent. Increasing the Cl/N ratio above about 9 had very little effect on hydrodenitrogenation activity.

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

A series of runs was made to test the effects of temperature and pressure on nitrogen removal, and runs were made at various space velocities to provide data to determine the reaction order. Basic conditions were 800° F., 1,000 psig, LHSV=1/2 and Cl/N=9.4 and conditions were varied around these basic conditions. The results of these tests are shown in Figures 11, 12 and 13.

As can be seen from Figure 11, the catalyst system is active over a relatively narrow temperature range from about 700 to 800° F. Over this range the removal changed from about 60 to 90 percent. Below

700° F. the nitrogen removal changed very little with temperature. However, temperatures below 572° F. were not investigated as being impracticable and high temperatures above 832° F. were not investigated because of reactor limitations. Increasing the temperature above 800° F. had little effect indicating that the last traces of nitrogen are extremely difficult to remove.

The effect of pressure at a constant temperature of 800° F. and a LHSV of 1/2 is shown in Figure 12. As would be expected, nitrogen removal was increased with pressure over the whole pressure range, increasing from about 62 percent at 200 psig to about 94 percent at 1,200 psig. However, above about 800 psi, at the higher conversions, the incremental effect of pressure was smaller, again indicating that the last bit of nitrogen is difficult to remove. Because of equipment limitations reactor pressure was not increased above 1,200 psig.

The effect of space velocity at constant temperature and pressure is shown in Figure 13 which shows the reciprocal of the concentration of nitrogen in the product oil as a function of reciprocal space velocity. A plot of this nature should yield a straight line if the reaction were pseudo-second order. The same data are also shown in Figure 14 where the logarithm of the ratio of the concentration of nitrogen in the product oil to the concentration in the feed is plotted against reciprocal space velocity. In this type of plot a straight line would result if the reaction were pseudo-first order as has been reported in

the literature. As can be seen from Figure 13, a fairly good straight line results indicating a 2nd order reaction. However, behavior like that shown in Figure 14 has been noted by other workers and has been explained by the formation of nitrogen containing by-products which are harder to denitrogenate than the original nitrogen compounds.[10]

The method of nitrogen removal appeared to be different at the lower temperature and pressures and to some extent at the higher space velocities. Under these conditions some of the nitrogen left the reactor combined in a heavy viscous material which was insouble in the product oil. Visual inspection of the reactor precooler showed that less NH_4Cl was formed under these conditions. This material was probably the hydrochlorides of hydrogenated intermediates of the nitrogen compounds in the oil.

I. Comparison of Chloride Catalysts With Other Hydrodenitrogenation Catalysts

A comparison of the nitrogen removal obtained using the chloride system with that obtained using other hydrodenitrogenation catalysts was made at 800° F., 1000 psig and LHSV=1/2 using CR#5 as the test oil. CR#5 was used for this comparison because data were available using this oil in testing various other catalysts and a direct comparison could be made. These data are shown in Figure 15 which shows the nitrogen removed as a function of time for a catalyst containing 7.3 percent nickel with a Cl/N ratio of 9.4, a catalyst containing 5.9

percent nickel and 15.5 percent tungsten in sulfided form, a catalyst containing 13.3 percent nickel in sulfided form, and Houdry series "C", a commercial cobalt molybdate catalyst. The data on the nickel tungsten sulfide catalyst were reported by Falk.[9] As can be seen from the figure, the chloride system is considerably more active than the cobalt molybdate catalyst and somewhat more active than the nickel tungsten sulfide catalyst, the nitrogen removal being 93, 85, and 80 percent respectively for the three catalysts at the end of about 48 hours on stream. At the same time the sulfided NiO catalyst with no HCl present removed only about 38 percent of the nitrogen.

J. Pure Component Studies

Several runs were made using synthetic mixtures in which pure nitrogen compounds were blended with an oil of low impurity level. Indole and quinoline were blended in "Peneteck", a highly refined Pennsylvania white oil, to give a nitrogen content of 0.3 percent, the level of nitrogen in the other test gas oil. These mixtures were denitrogenated at temperatures of 700 and 800° F., at 1000 psig and a Cl/N ratio of 9.0 at various space velocities in order to obtain rate data. Again the catalyst containing 6.1 percent nickel was used. These data are plotted in Figures 16 and 17 which shows the percent nitrogen removed as a function of space velocity for the two temperatures. Again it would appear that the reaction is 2nd order. Nitrogen removal was high for both compounds at both temperatures and all space

velocities. At 800° F. the nitrogen removal was over 99 percent at the lower space velocities and decreased to about 98 percent at a space velocity of 2 for both compounds. At 700° F. the nitrogen removal from the quinoline was 99+ percent for all except the run at a space velocity of 2. At this rate analysis showed 97.8 percent removal. At this temperature 97.6 percent of the nitrogen was removed from the indole at a space velocity of 1/4 but this decreased to 93.3 percent at a space velocity of 2. Again, at the lower temperature the method of nitrogen removal appeared to be different than at the high temperature. At 700° F. very little NH_4Cl accumulated at the reactor outlet. Under these conditions most of the nitrogen was removed combined in the heavy viscous material that was insoluble in the oil. Based on the experience from the gas oil studies this material was assumed to be the hydrochlorides of either the original nitrogen compounds or hydrogenated intermediates. At 800° F. it appeared that nearly all of the nitrogen left the reaction zone in the form of ammonium chloride.

The surprising result is that, at 800° F. the rate of removal of quinoline was about the same as that of indole while at 700° F. the rate of removal of quinoline was higher than that of indole. This is contrary to hydrodenitrogenation rate data reported in the literature.(10)

III. DESULFURIZATION

The catalysts now commercially used for hydrodenitrogenation were developed for hydrodesulfurization purposes. In using them for denitrogenation the reaction temperature and pressure must be increased considerably over that required for desulfurization and, as a result, during hydrodenitrogenation nearly all of the sulfur is removed from the feed oil. Since the oil used in the denitrogenation tests contained 0.858 wt. percent sulfur, all samples were analyzed for sulfur to determine the effect that the various catalyst and operating variables had on desulfurization. The results are rather surprising considering the high denitrogenation activity obtained with the NiCl-HCl catalyst system.

For all operating conditions the sulfur removal was quite low, the highest removal being about 87 percent at 800° F. and 1200 psig. The trend of sulfur removal generally followed the nitrogen removal quite closely only at a lower level. The sulfur removal as a function of the various catalyst and operating variables is shown in Figures 18 through 22.

As can be seen from Figures 18 and 19, a small amount of nickel and a small amount of chloride increased the sulfur removal considerably just as nitrogen removal was increased. The sulfur removal was increased from about 65 percent with no nickel on the catalyst and a Cl/N ratio of 9.4 to slightly over 80 percent when the catalyst contained 17.7 percent nickel, however the sulfur removal was nearly 80

percent when the catalyst contained only 0.9 percent nickel. With no chloride present, sulfur removal was only about 55 percent and was increased to about 70 percent when chloride sufficient to give a Cl/N ratio of 1.9 was added.

Increasing the Cl/N ratio above about 9.4 appeared to have no effect on sulfur removal.

Sulfur removal increased rapidly with temperature from about 10 percent at a reactor temperature of 572° F. to about 87 percent at 832° F. as shown in Figure 20. This was unlike nitrogen removal which leveled off at the lower temperature and has been explained by a different mode of nitrogen removal at the lower temperature. Other variables were constant at 1000 psig, LHSV=1/2 and Cl/N=9.4. At the higher temperature levels the incremental effect of temperature was lower than at the lower temperature levels.

As would be expected, sulfur removal was increased by increasing the reactor pressure, increasing from about 45 percent at 200 psig to about 87 percent at 1200 psig at 800° F. as shown in Figure 21. Increasing the pressure from 1000 psig to 1200 psig had very little effect on sulfur removal.

Figure 22 shows the effect of space velocity on sulfur removal at 800°F. and 1000 psig. Sulfur removal was decreased from about 88

percent at a space velocity of 1/8 to 57 percent at a space velocity of 2. A plot of reciprocal product concentration as a function of reciprocal space velocity resulted in a straight line indicating a pseudo-second order reaction. This is shown in Figure 23.

IV. HYDROCRACKING

Tests on the product oil showed that a considerable amount of cracking was taking place along with the denitrogenation. As a result, ASTM distillations were obtained on all products. The results are very interesting although no attempt was made to optimize or influence cracking in any way. The variation in product oil distillations with changes in the various operating variables is shown in Figures 24 through 29.

Since there is no absolute criteria for cracking activity, the effect that the different variables had on cracking will be discussed in qualitative terms only.

The effect of the type of metal impregnated on the catalyst on cracking activity is shown in Figure 24. This shows the distillation curves of the product oil from the preliminary hydrogenation runs when various metals were tried as denitrogenation catalyst at 800° F., 1000 psig, LHSV=1/4 and a Cl/N ratio=9.4. For comparison purposes the distillation of the oil obtained when no metal was added to the support alumina, and when the reactor was filled with alundum pellets only is also shown. As can be seen from the figure, a considerable amount of cracking was taking place at these conditions even with the low surface area alundum support. It also shows that metal type influences cracking greatly. Both manganese and strontium reduced the amount of cracking while nickel and cobalt increased the amount of cracking over that obtained when only the support alumina was used as a catalyst.

Figure 25 shows the effect that the catalyst composition has on cracking, other variables being held at 800° F., 1000 psig, LHSV=1/2 and a Cl/N ratio of 9.4. This shows that increasing the nickel content of the catalyst increased the cracking activity slightly and that a fairly large increase in cracking rate is obtained by adding a small amount of nickel. However, it appeared that cracking rate was not greatly increased when the nickel content was increased above this trace amount.

The effect that Cl/N ratio had on cracking while other variables were held at 800° F., 1000 psig, LHSV=1/2 and using a catalyst containing 6.1 percent Ni is shown in Figure 26. As would be expected, a small amount of chloride added with the feed increased the amount of cracking considerably, however cracking activity was not increased much when the amount of chloride that was added was doubled after the initial increment.

As would be expected, reactor temperature had a large influence on the cracking rate. This is shown in Figure 27 which shows the distillation of the products from runs made at various reactor temperatures when other variables were held at 1000 psig, LHSV=1/2 and Cl/N=9.4. At the lower temperatures it appeared that very little cracking was taking place and that probably some pure hydrogenation without cracking was occurring as shown by the increased boiling temperature of the product. The amount of light ends obtained increased rapidly with increasing temperature over the whole range of temperatures investigated.

Likewise, increasing reactor pressure and decreasing space veolocity increased the cracking activity over the whole range these variables were investigated as would be expected. This is shown in Figures 28 and 29. Again the basic reactor conditions were 1000 psig and Cl/N=9.4 and the catalyst contained 6.1 percent Ni.

V. GAS MAKE

A material balance was made on the reactor during a 12 hour period to give an idea of the amount of gaseous products being formed in the reactor. During a run at 800° F., 1000 psig, LHSV=1/2 and Cl/N=9.4 a material balance showed that about 93 percent of the feed material was recovered as product oil on a methylene chloride free basis. The difference of 7 percent was assumed to be the amount of gaseous products formed in the cracking reactions. Of course, a somewhat greater amount of gas was probably formed at the higher temperatures and pressures and lower space velocities, but material balances were not made during these runs.

The 7 percent gas make compares with a gas make of about 4.5 percent using a nickel tungsten sulfide catalyst during hydrodenitrogenation tests of CR#5 at the same temperature, pressure and space velocity.(9)

VI. CHLORINE IN PRODUCT OIL

All product samples were analyzed for residual chlorine since a chlorine compound, methylene chloride in most cases, was blended with the feed oil as a means of supplying HCl to the reactor. The quartz tube combustion method was used for the analysis.(2) In all cases the chlorine content was quite low ranging from 0 to 0.5 percent and it appeared that the means of adding chloride that is, methylene chloride, ethylene dichloride, or gaseous HCl had no effect on the amount of chlorine in the product. This indicates that the chlorine in the product

was there as a result of a chemical reaction involving gaseous HCl. The product from the reaction at 800°F., 1000 psig, LHSV=1/2 and using a Cl/N=9.4 contained 0.36, 0.31 and 0.29 wt. % chlorine when methylene chloride, ethylene dichloride and gaseous HCl were used respectively. In some cases however, there was a trend which indicated that certain operating variables had some effect on the amount of chlorine in the product. This is shown in Figures 30 and 31 which show the weight percent chlorine in the product as a function of the various operating and catalyst variables. As can be seen from Figure 30 (a) and (d), it appeared that catalyst composition and reactor pressure had no effect on the amount of chlorine in the product, the amount of chlorine being about 0.4 percent for all values of these variables. However, there was a definite increase in chlorine content of the product from 0 percent at 572° F. to about 0.4 percent at 832° F. when the other variables were held at 1000 psig, LHSV=1/2 and Cl/N=9.4. Also, as would be expected, the amount of chlorine in the product increased when the amount of chloride fed to the reactor was increased as shown in Figure 30(b). The chlorine found in the product increased from 0 percent when no chloride was fed to about 0.5 percent when the Cl/N ratio was maintained at 18.8. The effect of space velocity is shown in Figure 31. This figure shows that at the low space velocities there is more chlorine in the product oil than at the high space velocities, again indicating that the chlorine is in the product as a result of a chemical reaction. At a LHSV of 1/8 there was 0.56 percent chlorine in the

product while there was only 0.33 percent at a space velocity of 2.

VII. CATALYST LIFE

A long run was made to test the life of the catalyst. It was made in a series of 3 day runs since this was the longest continuous run that could be made before the reactor outlet plugged up with ammonium chloride. After 3 days on stream the reactor was cooled, dismantled and cleaned. The same catalyst was then recharged to the reactor and the run continued. Using this procedure the life of a catalyst containing 6.1 percent nickel was tested at 800° F., 1000 psig, LHSV=1/2 and a Cl/N ratio of 9.4.

The results of this test are shown in Figure 32. As can be seen, the activity of the catalyst started off at a high level with about 92 percent nitrogen removal but declined to about 88 percent over a 2 day period. The conversion was then constant at 88 to 89 percent through the 7th day. It then dropped to about 78 percent over the next three days where it remained for the rest of the test.

After 20 days of operation, the catalyst was regenerated in the reactor by burning in a stream of air at about 950 to 1000° F. over a 36 hour period. It was then reduced in a stream of hydrogen for about 16 hours at 850° F. and tested again in the usual manner.

By this regeneration, the initial activity of the catalyst was increased to a point where the nitrogen removal was 91 percent. Activity

then declined over a 8 day period to a point where only about 80 percent of the nitrogen was removed. At this time the life study was terminated.

VIII. DISCUSSION

A. Hydrodenitrogenation

At the optimum conditions, the nitrogen from the test oil left the reaction zone in the form of NH_4Cl. This material is dissociated at the temperature in the reactor and is deposited on the walls of the product cooler upon leaving the reactor (sublimation temperature = 635° F.). At lower reactor temperatures, lower pressures, higher space velocities, and with no nickel on the alumina pellets a considerable amount of the nitrogen was removed combined in a heavy, viscous material that was insoluble in the product oil. Under these conditions visual inspection of the reactor outlet showed that less NH_4Cl was formed. Although positive identification of the material was not made, in all probability it was the insoluble hydrochlorides of various nitrogen compounds formed in the reactor. The material contained 3.9 weight percent nitrogen and 11.4 weight percent chlorine and gave reactions characteristic of quaternary ammonium salts.[7] This composition gives a weight ratio of Cl/N=2.80, slightly more than a ratio of 2.50 which would result if each nitrogen atom were combined with one chlorine atom. Thus it would appear that the denitrogenation reaction using this system goes through some hydrochloride intermediate.

As mentioned previously, pure component hydrodenitrogenation studies have been conducted which suggest that the following mechanism is probable when the hydrodenitrogenation of quinoline is carried out in

the presence of a cobalt molybdate catalyst:[8]

(1) The first step is the chemisorption of the nitrogen compound onto an "active site". The active principle of the catalyst is pictured to function as an acid. The chemisorption is due to the interaction of the basic function of the nitrogen compound with the acid function of the catalyst. The chemisorbed compound then reacts with adsorbed molecular hydrogen to form intermediate nitrogen compounds.

(2) Further catalytic hydrogenation results in cleavage of the heterocyclic ring to form an alkyl aniline.

(3) The chemisorption of the alkyl aniline by the acid function of the catalyst results in the formation of an anilinium ion. This ion exerts a strong electron attraction and renders the carbon-nitrogen bond susceptible to the electrophilic attack of hydrogen. This results in the formation of an hydrocarbon and ammonia. This step is a simple hydrocracking reaction.

(4) The last step is the desorption of the products from the pores of the catalyst.

A rate expression derived from a theoretical consideration of this mechanism proved to fit experimental data when it was used as an

empirical equation. This same work showed that the rate controlling step of the reaction at 830° F. was the adsorption of quinoline, however, previous work between 725-775° F. showed that one of the surface reactions was controlling.[25]

Other workers[20,22] have shown that the chemisorption preference of the acid function of the catalyst is directly proportional to the relative basic strength of the nitrogen compound and that the chemisorption preference is such that the catalyst is effectively poisoned for compounds of less basic strength by the more basic nitrogen compounds.

In the preceding discussion the hydrodenitrogenation reaction was pictured as taking place on a single site and that the principal function of the catalyst was that of an acid. However, more recent work suggests that hydrotreating catalysts are "dual functional" and that reaction mechanisms using these catalysts involve migration of chemical intermediates between metal and acid sites of the catalyst.[4,11,29,30] This migration is such that the sites can be separated by macroscopic distances and still work.[30,31] It is suggested that the migrating species is a definite chemical compound although probably present in immeasurable quantities.[30] However, Ryffel[25] showed that, at low levels of nitrogen removal, the chemical intermediates that would be expected during the hydrodenitrogenation of quinoline using a cobalt molybdate catalyst were present in considerable concentrations. He found a considerable amount of tetrahydroquinoline and alkyl anilines

in the product oil under these conditions.

Thus, using the dual-functional approach, the reaction mechanism could be pictured as being essentially the same as above except that migration of intermediates between metal and acid sites occur.

In light of these mechanisms it is easy to picture reaction mechanisms which would account for the hydrodenitrogenation activity of the supported $NiCl_2$-HCl system. However, it was beyond the scope of this work to make an involved study of reaction mechanisms and only a conjectural discussion of the possibilities will be made.

It is probable that the $NiCl_2$-HCl catalyst system is just a dual functional catalyst and the two functions are metal (hydrogenation) and HCl (acid). However, since excess HCl is present and this material can combine with nitrogen bases present, the function of the HCl is not clear cut. Thus two of the possibilities are:

(1) The catalyst is the impregnated $NiCl_2$ and that excess HCl is required to maintain the active catalyst species.

(2) The catalyst system is impregnated nickel and gaseous or adsorbed HCl.

If the former were the case, the nickel would provide hydrogenation sites, the combined chlorine the acid sites. This does not appear to be the case, however, since a NiO-HCl system was quite active too, although it was not as active as when the metal was impregnated as the

chloride. About 85 percent of the nitrogen was removed using the NiO-HCl system compared with about 92 percent using the $NiCl_2$-HCl system. The lower activity observed when the NiO-HCl system was tested could be attributed to a reduced surface area of the NiO catalyst resulting because of the calcination of the catalyst at a high temperature during preparation. Thus it would appear that gaseous or adsorbed HCl is necessary for the high activity rather than having the chlorine combined with the nickel.

Hence it is probable that the catalyst system is impregnated nickel and gaseous or adsorbed HCl. The function of the nickel is undoubtedly to catalyze hydrogenation of the nitrogen compounds to intermediates which can be hydrocracked to the hydrocarbon and ammonia. Of course, with excess HCl present, hydrochlorides of these intermediates will form and the nickel will probably have a role in the hydrogenation of these compounds. However, the HCl could have several functions any or all of which could be important. It undoubtedly furnishes the acid sites required for the hydrodenitrogenation reaction, but it could also have a beneficial effect by eliminating strong chemisorption of product ammonia or of the strong nitrogen bases by tying them up as hydrochlorides. This would free the catalyst surface for the reaction of less basic compounds. Another possibility is that the intermediate hydrochlorides are themselves susceptable to the electrophilic attack of hydrogen. This would eliminate the need for a catalyst surface for

this part of the reaction.

It would take a detailed study to determine the actual mechanism however, based on the experimental results obtained in this study some conclusions can be made.

Figure 6 shows that a small amount of nickel increases the catalyst activity markedly when there is sufficient HCl present. Since nickel is a good hydrogenation catalyst it would appear that hydrogenation is an important step in the reaction mechanism. With no nickel present on the alumina there was considerable nitrogen removal, however most of it appeared to be combined in the insoluble material mentioned previously. With nickel in the catalyst the nitrogen left the reactor in the form of ammonium chloride. Thus, with nickel present to catalyze hydrogenation, it would appear that the hydrodenitrogenation reaction goes to completion while without nickel present hydrogenation is not complete. In the latter case it would appear that the nitrogen compounds end up at some intermediate stage. This tends to substantiate the contention that the purpose of the nickel is to give hydrogenation activity.

This also probably eliminates the possibility that the hydrochlorides themselves can be converted to the hydrocarbon and ammonia without the aid of the catalyst surface. Otherwise, nitrogen removal as NH_4Cl would have been higher than observed during the run with no nickel on the catalyst since a large amount of the insoluble material was formed in this run.

The overall reaction rate appears to be highly dependent upon HCl concentration up to a point as shown in Figure 10. This figure also shows that a large excess of HCl over the stoichiometric amount required for combination with nitrogen is required for high activity. Above a Cl/N ratio of about 9 no further activity was gained. It is possible that the step requiring chloride is reversible and that a high concentration of HCl is required to shift the equilibrium to a more favorable value. Another possibility is that there is an optimum number of acid sites required for the reaction; that a certain HCl concentration is required to furnish these sites and that no benefit is gained by furnishing more. This increased activity resulting from increased HCl concentration would be expected since it has been reported that, for dual functional catalysts, reactions occurring on the acidic sites are generally rate controlling.[31] Also, this same type of behavior has been shown to exist in other catalysts. In many cases catalyst composition studies have shown that increasing the metal content of a catalyst increases activity up to a point, while a further increase has no effect or reduces activity.[5,9,14] The same type of behavior is possible with the $NiCl_2$-HCl system.

The change in activity with temperature is characteristic of sulfide catalysts, that is, the catalyst is active over a rather narrow temperature range.[29] Above about 800° F. the nitrogen removal was increased very little with increasing temperature. This is probably

due to two factors. First, the last trace of nitrogen is difficult to remove by hydrodenitrogenation because of the formation of nitrogen containing by-products which are harder to denitrogenate than the original compounds[10]; and secondly, increasing temperature acts in such a way as to shift the thermodynamic equilibrium to a less favorable value.[27]

Apparently the higher temperature is needed for the final hydrocracking reactions in which the C-N bond is broken since the reaction at the lower temperature produced a considerable quantity of the insoluble complex.

Several runs were made using quinoline and indole blended in an oil of low impurity level to determine the behavior of representative basic and non-basic nitrogen compounds to the catalyst system. At 800° F. nitrogen removal was nearly 100 percent at a space velocity of 1/4 and dropped to only about 98 percent when the blends of both quinoline and indole were denitrogenated using a catalyst containing 6.1% Ni and a Cl/N=9.0. Nitrogen removal was nearly identical for each compound. During these tests it appeared that all of the nitrogen was converted to ammonium chloride. These data are in contrast to other experimental data which have shown that the rate of removal of indole is about 4 times that of quinoline.[10] Another set of runs was made at 700°F. and in this case the removal of nitrogen was higher from the quinoline than with indole although at this lower temperature the mode

of removal was different in that insoluble hydrochlorides were formed in both tests. It appeared that the only difference was that the formation of the insoluble material was more complete in the test using quinoline. The nitrogen removal as a function of space velocity for both temperatures is shown graphically in Figures 16 and 17.

These data would indicate that at higher temperatures, where the hydrogenation reactions can take place, the relative basic strength of the nitrogen compounds has little effect on the rate of hydrodenitrogenation. Otherwise there would have been a significant difference in the rate of removal of quinoline and indole. The data at the lower temperature would indicate that some hydrogenation of the compounds is taking place at the lower temperatures since indole itself is not basic while the hydroindoles and indolines are. Since little NH_4Cl was formed at the low temperature, it would appear that the higher temperatures are required for the cleavage of the heterocyclic ring and/or the breaking of the carbon-nitrogen bond.

Runs were made at various space veolcities at the optimum reactor conditions to determine the order of the reaction. A plot of reciprocal product nitrogen content as a function of reciprocal space velocity resulted in a straight line, indicating that the reaction is pseudo-second order. However, these same data, when tested for a first order reaction, exhibited the same behavior as that reported by Flinn and co-workers.[10] That is, a straight line resulted for the lower nitrogen

removal at the higher space velocities and another straight line resulted at the higher level of denitrogenation but with a much lower slope. This indicates a lower reaction rate constant for the higher levels of nitrogen removal. This phenomena has been explained by Flinn as resulting from the formation of by-product nitrogen compounds in the reactor which are harder to denitrogenate than the original compounds.

Other workers have also reported the hydrodenitrogenation reaction to be pseudo-second order and without analytical data on the type of nitrogen compounds in the oil before and after denitrogenation it would be impossible to choose the correct reaction order.

B. Hydrocracking

ASTM distillations obtained on all product samples showed that a considerable amount of hydrocracking was taking place along with the denitrogenation. This is not surprising since dual functional catalysts are used extensively as hydrocracking catalysts. Some of the more common hydrocracking catalysts are supported nickel tungsten sulfide,[6,29] supported cobalt sulfide[14,29] and platinum or nickel supported on an acid silica-alumina cracking catalyst.[4] The same type of catalyst is used for both hydrodenitrogenation and hydrocracking, however in using them as denitrogenation catalysts the catalyst is effectively poisoned for hydrocracking by the nitrogen compounds and as a result extensive hydrocracking does not take place. This poisoning

is clearly shown by Jacobson's example mentioned in the introduction[14] and by Falk's data.[9] The nickel tungsten sulfide catalyst used by Falk is also used extensively as a hydrocracking catalyst[9] and as a catalyst for splitting coal tar.[29] Apparently, the poisoning is brought about by the strong chemisorption of the basic nitrogen compounds which renders the acidic sites inactive. These acid sites are necessary for the cracking reactions to take place. However, using the Ni-HCl system there is every reason to believe that this strong chemisorption is reduced or eliminated and that, with excess HCl present, a deficiency of acid sites should not exist even with a large quantity of nitrogen compounds present. Thus it would seem that a considerable amount of hydrocracking should take place along with the denitrogenation. This appears to be the case as shown in Figures 24 through 29 which show the effect that various operating conditions have on cracking.

A direct comparison with commercial hydrocracking processes cannot be made since data reported in the literature generally are for multipass hydrocracking operations at different conditions and using a somewhat heavier feed stock than the test oil used in this work.

The role of the metal and acid sites of the dual functional catalysts are somewhat different during hydrocracking than in hydrodenitrogenation. The principal role of the metal appears to be to keep the acidic sites free and active by the hydrogenation of compounds that may

form coke in the reaction [4] while, of course, the role of the acid sites is to catalyze cracking.

Initially, with sufficient HCl present, the hydrocracking activity was quite high even with no nickel present on the catalyst as shown in Figure 25. There was a fairly large increase in cracking rate brought about by adding a small amount of nickel indicating that the role of nickel is more than that mentioned above, however, activity was not greatly increased after this trace amount was added. These data were obtained from samples taken after about 48 hours on stream. During this time coke lay down would probably not affect activity much. However, if coking were a problem, the amount of nickel on the catalyst would probably have some effect on catalyst life.

A small amount of HCl added with the feed appeared to have a fairly large effect on the amount of cracking obtained as shown in Figure 26, and cracking activity appeared to increase somewhat with each additional increment of HCl added. This would be expected because, as mentioned previously, the reactions taking place on the acid sites have been shown to generally be rate controlling. There was considerable cracking activity with no added HCl, but this was probably due to the acid sites available from the original support and from the chlorine in the impregnated metal salt, $NiCl_2$, which would form some HCl in the hydrogen atmosphere.

The amount of cracking was increased greatly by increasing the temperature and pressure and by decreasing the space velocity as would be expected.

The gas make was determined at 800° F., 1,000 psig, LHSV=1/2, Cl/N=9.4 using a catalyst containing 6.1% Ni by material balance on the reactor and found to be about 7 percent by weight. This compares with about 4.5 percent using nickel tungsten sulfide as a hydrodenitrogenation catalyst using a similar oil (CR#5) at the same conditions. Thus it appears that the gas make using the Ni-HCl system is considerably higher than when denitrogenation is carried out using a conventional catalyst. The gas make at other conditions was not determined.

C. Desulfurization

The hydrodenitrogenation catalysts now used commercially were developed for desulfurization. However, the conditions required for denitrogenation are much more severe than those required for desulfurization and, as a result, nearly all of the sulfur present in the oil is removed along with the nitrogen when these catalysts are used for denitrogenation. This was not the case using the Ni-HCl catalyst system, however.

Sulfur removal was generally quite low and at the optimum denitrogenation conditions it was only about 80 percent, much lower than would be expected if a conventional hydrotreating catalyst were used. This

high denitrogenation activity and low desulfurization activity must reflect the affinity that the basic nitrogen compounds have for the HCl. Since the sulfur compounds are in general themselves acidic, a high desulfurization activity would not be expected using the highly acidic catalyst. Indeed, mechanism studies on the hydrodesulfurization of thiophene in the presence of a cobalt molybdate catalyst indicate that the metal, Mo, of an exposed plane of MoS_2 is the active desulfurization catalytic species while the active species[19] for denitrogenation has been identified as being an acid. For this system then, the desulfurization is probably due to reaction on the nickel sites and due to pure hydrocracking reactions taking place on the acid sites. This is indicated by the increase in desulfurization activity with nickel content and with the amount of chloride fed.

D. Chlorine in Product Oil

All product samples were analyzed for chlorine to determine the effect that the various operating and catalyst variables had on the amount of chlorine remaining in the product.

The form of chloride fed to supply the HCl seemed to have little effect on the amount of residual chlorine. At comparable reactor conditions and at a Cl/N ratio = 9.4 the product contained 0.36, 0.31, 0.29 weight percent chlorine when CH_2Cl_2, $C_2H_4Cl_2$ and gaseous HCl was fed to the reactor, respectively. This indicates that the chlorine in the product is due to formation by chemical reaction rather than

from non-decomposed methylene chloride. This is also indicated by Figure 30 b, c and Figure 31 which shows the chlorine in the product as a function of the chloride concentration in the feed, the reactor temperature, and the space velocity. These data show that the amount of chlorine in the product increases with the amount of chlorine fed, and with temperature while it decreases with space velocity. This again indicates that the residual chlorine is due to formation by chemical reaction in the reactor. The amount of nickel on the catalyst and the reactor pressure appeared to have no effect on the amount of chlorine in the product.

The residual chlorine compounds are rather unstable as shown by their decomposition during distillation of the product. There was a strong smell of HCl early in the ASTM distillations indicating that decomposition was taking place as the compounds were vaporized. This is a behavior characteristic of hydrochlorides and probably means that the chlorine is combined in a small amount of soluble hydrochlorides of stable nitrogen bases.

E. Catalyst Life

In order for a denitrogenation catalyst to be useful for a commercial operation, it must be active for a long period of time. Also, ideally, it should be possible to regenerate the catalyst when the activity has dropped to such a level that it is no longer economically feasible to continue using it at the low activity level. For

this reason a long run was made to test the life of $NiCl_2$-HCl catalyst system and, after a reasonably long run, the catalyst was regenerated. The long run was carried out in a series of 3 day runs because this was the maximum time that the reactor could be operated continuously before the reactor precooler plugged up with solid NH_4Cl. After each 3 day period the reactor was shut down, allowed to cool overnight, dismantled and cleaned. The original catalyst was then recharged to the reactor and the run continued. During the 28 day run it was necessary to shut down and clean the reactor 10 times.

In this run the nitrogen removal started off at about 92 percent but declined over a two day period to about 89 percent where it remained essentially constant for the next 7 days. It then dropped over the next 3 day period to about 79 percent where it remained about constant at 77 to 79 percent through the 20th day.

After 20 days of operation the catalyst was regenerated by passing a stream of air over it in the reactor at 950 to 1000° F. over a 36 hour period. The catalyst was then reduced by passing hydrogen over it for about 16 hours at 850° F. and finally tested again in the usual manner. Regeneration increased the activity to a point where initially 91 percent of the nitrogen was removed. This dropped to about 80 percent over the next 8 day period when the life study was terminated.

Visual inspection of the catalyst each time the reactor was cleaned showed that there was a considerable coke lay-down on the catalyst and

the decline in activity can probably be attributed to this coking. Apparently a certain coke lay-down can be tolerated before a noticeable decline in activity is experienced as shown by the constant activity for the first few days. It is probable that after a certain coke lay-down is reached the pores of the catalyst start to plug up thus reducing the effective surface area of the catalyst and the number of nickel sites available for the reaction to take place.

The activity recovery brought about by the regeneration procedure also indicated that coking was the main cause of the activity decline.

Thus, it would seem that anything that would reduce coke formation would increase catalyst life. For example, reducing temperature, increasing hydrogen partial pressure, and increasing the amount of nickel on the catalyst.

F. General Discussion of the Feasibility of the System

The first tests using the Ni-HCl catalyst system were carried out in a stainless steel reactor but corrosion of the reactor was so rapid that the thermowell burst at the reactor pressure after only a few days of operation. For this reason a new reactor was fabricated from Inconel alloy 600 and used in subsequent tests.

Corrosion was still appreciable using this reactor, however, and the thermowell corroded through after about the equivalent of 100 days of continuous operation and had to be replaced.

Corrosion was also severe in the cold section of the reactor. A monel screen was placed at the reactor outlet to prevent NH_4Cl from reaching the back pressure control valve. This screen was severely corroded and had to be replaced periodically.

From this it would appear that the corrosion problem alone would prevent this system from being economically attractive unless a reactor system could be made which would have better corrosion resistance than the Inconel alloy.

The accumulation of NH_4Cl at the reactor outlet would bring about operation difficulties although it may be possible to design a system in which the NH_4Cl could be washed periodically from the cooler with water. Continuous operation probably would not be possible at lower pressures since at the sublimation temperature of NH_4Cl (635° F.) (necessarily the temperature in the precooler) a pressure of about 2000 psi would be required to maintain water in the liquid state. Thus, at higher pressures, a continuous washer might be practical.

Of course, the chief disadvantage that would have to be overcome would be the fairly rapid decline in activity due to coking. In order for the system to be economically attractive the catalyst would have to remain active considerably longer than the time observed in the life study. Of course, some of the decline noted in the test could have been due to the frequent exposure of the catalyst to air during the reactor cleaning and it may be that catalyst life during a

continuous run would be longer. Also, there are probably ways that the catalyst life could be made longer if the decline was due to coke lay-down. For example, increasing pressure and decreasing temperature would probably extend catalyst life by cutting down on the amount of coking with no decrease in denitrogenation activity. Another possibility would be to add more nickel to the catalyst. This would make more hydrogenation sites available and promote the hydrogenation of coke precursors which would extend catalyst life. Also, a catalyst support which would make the catalyst less acidic would cut down on the amount of cracking and hence on the amount of coke lay-down. This could be done by using alumina instead of the acidic silica alumina support.

Regeneration of the catalyst by burning the coke from it in a stream of air followed by reduction with hydrogen appeared to result in complete recovery of the original catalyst activity. In fact, after the one regeneration, initial activity was greater than that observed initially in the first day of operations using the original catalyst. Hence, it would appear that regeneration of the catalyst would be no problem.

Life studies using other catalysts were not made so it is not known how this test oil would affect the life of other catalysts but during the short 3 day tests, the Ni-HCl catalyst system was considerably more active than other hydrotreating catalysts. In fact, after

only three days on stream using the Houdry series "C" cobalt molybdate catalyst the product oil contained 735 ppm nitrogen when it was tested at the same conditions. This compares with about 650 ppm nitrogen left in the product oil during the latter part of the long run, before catalyst regeneration using the $NiCl_2$-HCl system.

Also, based on the results of the pure component studies, it would appear that essentially complete removal of nitrogen from a lighter gas oil could be obtained at much higher space velocities than would be possible using conventional catalysts.

Thus, if operating and catalyst conditions could be changed so that the high activity could be maintained for longer periods between regeneration, the system would be attractive. Of course, the high denitrogenation activity would be the main advantage but there would also be distinct advantages in the manufacture of the catalyst since lengthy and expensive calcination and sulfiding steps would not be required as is the case in the manufacture of a cobalt molybdate catalyst.

IX. CONCLUSIONS

1. An alumina supported nickel-HCl catalyst system has been shown to be extremely active with respect to hydrodenitrogenation. This catalyst system gave 10 to 15 percent more nitrogen removal than a commercial cobalt molybdate catalyst at the same conditions when it was tested using a high nitrogen content heavy California gas oil which contained 0.315 percent nitrogen. It was also somewhat more active than a nickel tungsten sulfide catalyst. An alumina supported $CoCl_2$-HCl catalyst system also gave excellent results although the one catalyst tested was slightly less active than the nickel catalyst. $SrCl_2$ and $MnCl_2$ catalysts were relatively inactive.

2. The optimum reactor conditions for denitrogenation for the particular heavy gas oil tested appeared to be:

Catalyst:	>	4% Ni ($NiCl_2$)
Temperature	=	800° F.
Pressure	=	1000 psig
Cl/N	>	9 atom/atom

3. The catalyst was very active for only about a 7 day period. During a long run the activity dropped over a 10 day period to a point where only about 79 percent of the nitrogen was removed. Nitrogen removal was constant at about 79 percent for the remainder of a long run before regeneration, 20 days in all. The decline in activity appeared to be due to coke formation on the catalyst pellets.

In contrast, the activity of a cobalt molybdate catalyst was reduced to a point where only about 75 percent of the nitrogen from

the test oil was removed after only 3 days of operation at the same conditions using the same test oil.

4. The catalyst can be regenerated using air followed by reduction in a hydrogen atmosphere. This regeneration appears to restore the original activity of the catalyst.

5. The catalyst system showed only moderate activity for desulfurization at the reactor conditions and catalyst compositions investigated. At the optimum denitrogenation conditions only about 80 percent of the sulfur was removed from the test oil which contained 0.858 percent sulfur.

6. The catalyst system appears to have considerable hydrocracking activity and as such appears to be resistant to poisoning by nitrogen and sulfur compounds although coke lay-down rate appears to be high. Gas make was about 7 percent at 800° F., 1000 psig, Cl/N= 9.4 atom/atom and a LHSV=1/2 using a catalyst containing 6.1 percent nickel on a 6 percent SiO-alumina support.

7. The atmosphere in the reactor using this system is very corrosive. Rapid corrosion of a stainless steel reactor was experienced while the corrosion rate of an Inconel alloy 600 reactor was moderate during catalyst tests.

X. RECOMMENDATIONS

Several possible avenues of research arose during the course of this work which could not be investigated because of time limitations. Some of the more interesting possibilities are listed below. It is recommended that these be investigated in the future.

1. HCl may be a general means of increasing the activity of conventional hydrodenitrogenation catalysts since it appears that a small amount of HCl eliminates strong chemisorption of the nitrogen bases. It is recommended that these catalysts be tested using a small amount of HCl in the feed in a reactor system similar to the one used in this study to determine the effect on activity.

2. A small amount of HCl added to the feed may eliminate nitrogen poisoning of conventional hydrocracking catalysts. It is recommended that tests of hydrocracking catalysts be made using a high nitrogen content oil with and without added HCl and a comparison be made using nitrogen free test oils.

3. Catalyst life studies using the Ni-HCl system at higher pressures and lower temperatures should be made to find the effect that these variables have on catalyst life and coke lay down. A study should also be made to determine the optimum regeneration procedure.

4. An investigation of other schemes of operation using the Ni-HCl catalyst system together with a conventional hydrotreating system would be interesting. One such system might be to:

(a) Treat the oil at a low temperature and pressure with gaseous HCl and hydrogen over the $NiCl_2$ catalyst to remove part of the nitrogen as the insoluble complex. Presumably this would remove the more basic nitrogen compounds which are harder to denitrogenate. Then

(b) treat the product from stage (a) using a conventional hydrotreating catalyst and methods.

It is very possible a significantly increased overall nitrogen removal would result.

Other treating schemes that could be beneficial are obvious.

5. An investigation of other means of adding acid sites to a hydrodenitrogenation catalyst would be interesting, for example using other hydrohalogen acids.

XI. APPENDIX

TABLE IV

Physical and Chemical Properties of Catalyst Support Used in All But Preliminary Catalyst Tests

Source:	The Harshaw Chemical Company
Company Designation:	AL-1802-E 1/8" alumina catalyst
Properties:	1/8" extrusions
	92% Al_2O_3, 6% SiO_2
	Surface Area = 277 m^2/gr
	Pore Volume = 0.91 cc/gr
	Apparent Bulk Density = 33#/ft^3

TABLE V

Properties of Test Oils

Sample Designation	CR #5	CR #6
API Gravity	21.3	20.4
ASTM D-158 (*)		
IBP	593	613
5%	640	650
10%	657	663
20%	677	679
30%	693	692
40%	707	703
50%	722	714
60%	735	725
70%	750	734
80%	760	737
90%	-	746
95%	-	-
E.P.	-	-
Wt. % Nitrogen	0.318	0.315
Wt. % Sulfur	0.815	0.858

Notes: (*) Distillation at atmospheric pressure, Bozeman, Montana, about 640 mm Hg.

TABLE VI

Experimental Data

RUN NO.			41	52	53	54-2	55
A. Reactor Conditions*							
1. Temperature-°F.			800	800	800	800	800
2. Pressure-PSIG			1000	1000	1000	1000	1000
3. LHSV Hr^{-1}			1/4	1/4	1/4	1/4	1/4
4. Feed			CR#5	CR#5	CR#5	CR#5	CR#5
5. Catalyst**			8.0% Mn.	6.4% Sr.	6.0% Co.	7.0% Ni	Al-1802-E only
6. Cl/N Atom/Atom***			9.4	9.4	9.4	9.4	9.4
B. Product Properties		Feed(CR#5)					
1. API Gravity		21.3	26.5	26.0	32.0	34.4	28.4
2. ASTM Dist. D-158							
Temp. in	IBP	593	217	205	165	169	200
°F. at	5%	640	290	290	205	210	250
640 MM Hg	10%	657	335	333	240	238	282
	20%	677	441	447	278	277	344
	30%	693	524	553	330	316	421
	40%	707	581	607	407	367	491
	50%	722	624	644	503	423	550
	60%	735	655	670	566	485	614
	70%	750	684	689	640	555	670
	80%	760	706	727	697	617	720
	90%	-	751	760	745	679	755
	95%	-	-	-	-	725	-
	E.P.	-					
3. Wt. % Nitrogen		0.318	.0840	.0810	0.027	0.0104	0.0480
4. Wt. % Sulfur		0.815	0.304	0.388	0.184	0.125	0.233
5. St. % Chlorine		-	0.302	0.690	0.523	0.563	0.409
C. Impurity Removal							
1. % Nitrogen		-	73.0	74.5	91.2	96.6	84.9
2. % Sulfur		-	62.7	52.5	77.5	84.6	70.8

Notes: *All runs with H_2 rate of 5,000 SCF/bbl
**Metal Impregnated on Al-1802-E as chloride
***Chlorine from methylene chloride unless otherwise noted.

TABLE VI (Continued)

RUN NO.	56	57		58	59	60	61
A. Reactor Conditions*							
1. Temperature- °F.	800	800	-	800	800	800	800
2. Pressure - PSIG	1000	1000	-	1000	1000	1000	1000
3. LHSV Hr^{-1}	1/4	1/4	-	1/2	1/2	1/2	1/2
4. Feed	CR#5	CR#6	-	CR#6	CR#6	CR#6	CR#6
5. Catalyst**	Alundum Only	7.1% Co	-	7.3% Ni	AL-1802-E Only	4.2% Ni	0.9% Ni
6. Cl/N Atom/Atom***	9.4	9.4	-	9.4	9.4	9.4	9.4
B. Product Properties			Feed(CR#6)				
1. API Gravity	25.1	32.5	20.4	29.9	27.0	29.5	30.2
2. ASTM Dist. D-158							
Temp. in IBP	250	200	613	188	202	178	185
degrees F. 5%	334	232	650	265	294	251	251
at 640 MM Hg 10%	424	256	663	301	342	306	291
20%	564	300	679	368	428	384	380
30%	620	341	692	436	515	457	460
40%	650	388	703	504	572	520	521
50%	676	444	714	563	612	575	571
60%	697	500	725	604	646	614	613
70%	717	574	734	644	672	650	644
80%	740	631	737	675	699	680	670
90%	-	682	746	712	732	730	712
95%	-	725	-	740	746	750	-
E.P.	-	-	-	-	-	-	-
3. Wt.% Nitrogen	0.116	0.0193	0.315	0.0194	0.0864	0.0218	0.033
4. Wt.% Sulfur	0.405	0.119	0.858	0.163	0.296	0.167	0.177
5. Wt.% Chlorine	0.720	0.417	-	0.485	0.388	0.396	0.347
C. Impurity Removal							
1. % Nitrogen	63.4	94.0	-	94.0	73.5	92.8	89.5
2. % Sulfur	49.9	86.0	-	81.0	65.5	80.5	79.4

TABLE VI (Continued)

RUN NO.	62	63	64	64	64	64	64
A. Reactor Conditions*							
1. Temperature - °F.	800	800	800	800	800	800	800
2. Pressure - PSIG	1000	1000	1000	1000	1000	1000	1000
3. LHSV-Hr^{-1}	1/2	1/2	1/2	1/2	1/2	1/2	1/2
4. Feed	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6
5. Catalyst**	17.7% Ni	0.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.4	9.4	9.4	0	1.88	4.70	9.4
B. Product Properties							
1. API Gravity	30.6	29.0	29.8	-	28.9	29.5	29.8
2. ASTM Dist. D-158							
Temp. in degrees F. at 640 MM Hg IBP	186	190	184	215	188	184	184
5%	247	263	250	311	269	250	250
10%	283	309	305	381	318	308	305
20%	338	391	382	510	412	396	382
30%	417	461	456	587	488	476	456
40%	483	520	518	622	550	540	518
50%	531	576	570	652	597	585	570
60%	578	617	613	678	633	626	613
70%	638	652	646	698	662	657	646
80%	680	680	676	722	691	685	676
90%	710	703	728	752	729	722	728
95%	-	-	753	-	758	-	753
E.P.	-	-	-	-	-	-	-
3. Wt. % Nitrogen	0.0182	0.052	0.0194	.106	0.0807	.0535	0.0194
4. Wt. % Sulfur	0.155	0.229	0.193	0.381	0.262	0.230	0.193
5. Wt. % Chlorine	0.364	0.356	0.356	0.0875	0.142	0.254	0.356
C. Impurity Removal							
1. % Nitrogen	94.4	84.0	92.0	66.0	74.3	82.9	92.0
2. % Sulfur	82.0	73.3	79.5	55.7	69.5	73.3	77.5

TABLE VI (Continued)

RUN NO.	65	65	67	67	67	67
A. Reactor Conditions*						
1. Temperature - °F.	800	800	572	662	706	753
2. Pressure - PSIG	1000	1000	1000	1000	1000	1000
3. LHSV Hr^{-1}	1/2	1/2	1/2	1/2	1/2	1/2
4. Feed	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6
5. Catalyst**	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	14.1	18.8	9.4	9.4	9.4	9.4
B. Product Properties						
1. API Gravity	30.5	30.8	22.0	22.4	23.7	26.2
2. ASTM Dist. D-158						
Temp. in degrees F. at 640 MM Hg IBP	188	176	585	366	300	202
5%	265	252	634	617	504	325
10%	303	290	655	640	587	424
20%	369	354	679	667	643	542
30%	434	415	694	685	672	603
40%	495	476	707	698	690	640
50%	549	531	720	714	704	666
60%	596	580	732	723	720	687
70%	633	621	744	741	734	709
80%	668	658	756	-	-	730
90%	708	700	-	-	-	750
95%	732	735	-	-	-	-
E.P.	-	-	-	-	-	-
3. Wt. % Nitrogen	0.0247	0.0227	0.144	0.141	0.118	.0825
4. Wt. % Sulfur	0.196	0.191	0.777	0.599	0.482	0.294
5. Wt. % Chlorine	0.409	0.446	0	0.170	0.195	0.274
C. Impurity Removal						
1. % Nitrogen	92.0	93.0	54.3	55.0	62.1	74.0
2. % Sulfur	77.3	78.0	9.5	30.2	43.9	65.6

TABLE VI (Continued)

RUN NO.	65	68	69	69	69	70	64
A. Reactor Conditions*							
1. Temperature - °F.	800	832	800	800	800	800	800
2. Pressure - PSIG	1000	1000	200	400	600	800	1000
3. LHSV - Hr^{-1}	1/2	1/2	1/2	1/2	1/2	1/2	1/2
4. Feed	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6
5. Catalyst**	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.4	9.4	9.4	9.4	9.4	9.4	9.4
B. Product Properties							
1. API Gravity	29.8	31.8	23.9	24.7	25.5	27.5	29.8
2. ASTM Dist. D-158							
Temp. in degrees F. at 640 MM Hg IBP	184	170	224	218	226	198	184
5%	250	212	345	340	300	274	250
10%	305	244	450	426	390	343	305
20%	382	296	569	553	510	440	382
30%	456	353	617	610	580	507	456
40%	518	418	650	645	620	561	518
50%	570	480	671	668	650	606	570
60%	613	528	691	688	673	637	613
70%	646	560	710	707	693	664	646
80%	676	625	729	729	715	687	676
90%	728	700	-	756	-	725	728
95%	753	-	-	-	-	-	753
E.P.	-	-	-	-	-	-	-
3. Wt. % Nitrogen	0.0194	.0236	0.120	0.102	0.0786	.043	0.0194
4. Wt. % Sulfur	0.193	0.153	0.449	0.464	0.350	0.259	0.193
5. Wt. % Chlorine	0.356	0.406	0.360	0.328	0.503	0.554	0.356
C. Impurity Removal							
1. % Nitrogen	92.0	92.5	62.0	67.6	75.0	86.2	92.0
2. T Sulfur	79.5	82.1	47.6	46.0	59.4	69.7	77.5

TABLE VI (Continued)

RUN NO.	70	71	71	71	71	71
A. Reactor Conditions*						
1. Temperature - °F.	800	800	800	800	800	800
2. Pressure - PSIG	1200	1000	1000	1000	1000	1000
3. LHSV - Hr^{-1}	1/2	1/8	1/4	1/2	1	2
4. Feed	CR#6	CR#6	CR#6	CR#6	CR#6	CR#6
5. Catalyst**	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.4	9.4	9.4	9.4	9.4	9.4
B. Product Properties						
1. API Gravity	30.9	-	-	30.6	26.8	25.7
2. ASTM Dist. D-158						
Temp. in degrees F. at 640 MM Hg IBP	184	165	190	202	205	248
5%	270	233	244	269	290	346
10%	303	253	267	309	364	430
20%	368	285	304	370	461	550
30%	435	314	343	433	540	604
40%	487	340	389	493	590	643
50%	554	383	446	550	628	669
60%	597	438	512	596	658	692
70%	631	500	580	636	680	711
80%	670	568	639	670	-	734
90%	703	675	700	710	-	760
95%	-	703	720	735	-	-
E.P.	-	715	-	-	-	-
3. Wt. % Nitrogen	.0195	0.0	0.0142	0.0236	0.0670	0.126
4. Wt. % Sulfur	0.190	0.109	0.128	0.181	0.262	0.372
5. Wt. % Chlorine	0.386	0.566	0.425	0.382	0.360	0.332
C. Impurity Removal						
1. % Nitrogen	93.8	100	95.6	92.5	78.8	60.0
2. % Sulfur	77.9	87.4	85.0	78.9	69.6	56.6

TABLE VI (Continued)

RUN NO.	72	73	73	73	73	74	74
A. Reactor Conditions*							
1. Temperature - °F.	800	800	800	800	800	800	800
2. Pressure - PSIG	1000	1000	1000	1000	1000	1000	1000
3. LHSV - Hr^{-1}	1/2	1/4	1/2	1	2	1/4	1/2
4. Feed	CR#6	Note(2)	Note(2)	Note(2)	Note(2)	Note(3)	Note(3)
5. Catalyst**	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.4(1)	9.0	9.0	9.0	9.0	9.0	9.0
B. Product Properties							
1. API Gravity	29.9						
2. ASTM Dist. D-158							
Temp. in degrees F. at 640 MM Hg IBP	208						
5%	261						
10%	296						
20%	356						
30%	430						
40%	497						
50%	554						
60%	599						
70%	636						
80%	671						
90%	710						
95%	-						
E.P.	-						
3. Wt. % Nitrogen	0.0257	0.00258	0.00262	0.0052	0.0065	0.00	0.00131
4. Wt. % Sulfur	0.171	-	-	-	-	-	-
5. Wt. % Chlorine	0.310	-	-	-	-	-	-
C. Impurtiy Removal							
1. % Nitrogen	91.9	99.0	99.0	98.5	97.9	100	99.5
2. % Sulfur	80.1	-	-	-	-	-	-

Notes: (1) From $C_2H_4Cl_2$
(2) Feed - Peneteck + Indole, 0.3% Nitrogen
(3) Feed - Peneteck + Quinoline, 0.3% Nitrogen

TABLE VI (Continued)

RUN NO.	74	74	75	76	76	76
A. Reactor Conditions*						
1. Temperature - °F.	800	800	800	700	700	700
2. Pressure - PSIG	1000	1000	1000	1000	1000	1000
3. LHSV - Hr^{-1}	1	2	1/2	1/4	1/2	1
4. Feed	Note(3)	Note(3)	CR#6	Note(3)	Note(3)	Note(3)
5. Catalyst**	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.0	9.0	9.4(4)	9.0	9.0	9.0
B. Product Properties						
1. API Gravity			30.1			
2. ASTM Dist. D-158						
Temp. in degrees F. at 640 MM Hg. IBP			184			
5%			250			
10%			287			
20%			357			
30%			430			
40%			499			
50%			551			
60%			605			
70%			641			
80%			676			
90%			723			
95%			750			
E.P.			-			
3. Wt. % Nitrogen	0.0039	0.0065	0.031	0.0026	0.0017	0.0018
4. Wt. % Sulfur	-	-	0.180	-	-	-
5. Wt. % Chlorine	-	-	0.291	-	-	-
C. Impurity Removal						
1. % Nitrogen	98.5	97.5	90.0	99.0	99.5	99.4
2. % Sulfur	-	-	79.0	-	-	-

Note (3) Feed-Peneteck + Quinoline, 0.3% Nitrogen

TABLE VI (Continued)

RUN NO.	76	77	78	78	78	78
A. Reactor Conditions*						
1. Temperature - °F.	700	800	700	700	700	700
2. Pressure - PSIG	1000	1000	1000	1000	1000	1000
3. LHSV - Hr^{-1}	2	1/2	1/4	1/2	1	2
4. Feed	Note(3)	CR#6	Note(2)	Note(2)	Note(2)	Note(2)
5. Catalyst**	6.1% Ni	4.7% Ni(1)	6.1% Ni	6.1% Ni	6.1% Ni	6.1% Ni
6. Cl/N Atom/Atom***	9.0	9.4	9.0	9.0	9.0	9.0
B. Product Properties						
1. API Gravity		29.4				
2. ASTM Dist. D-158						
Temp. in degrees F. at 640 MM Hg IBP		209				
5%		274				
10%		307				
20%		370				
30%		470				
40%		537				
50%		587				
60%		627				
70%		660				
80%		689				
90%		731				
95%		760+				
E.P.		-				
3. Wt. % Nitrogen	0.0065	0.0455	.0065	0.0120	.0156	.0195
4. Wt. % Sulfur	-	0.195	-	-	-	-
5. Wt. % Chlorine	-	0.466	-	-	-	-
C. Impurity Removal						
1. % nitrogen	97.8	85.3	97.6	96.0	94.6	93.3
2. % sulfur	-	77.5	-	-	-	-

Notes: (1) Nickel on Alumina as NiO
(2) Feed - Peneteck + Indole, 0.3% Nitrogen

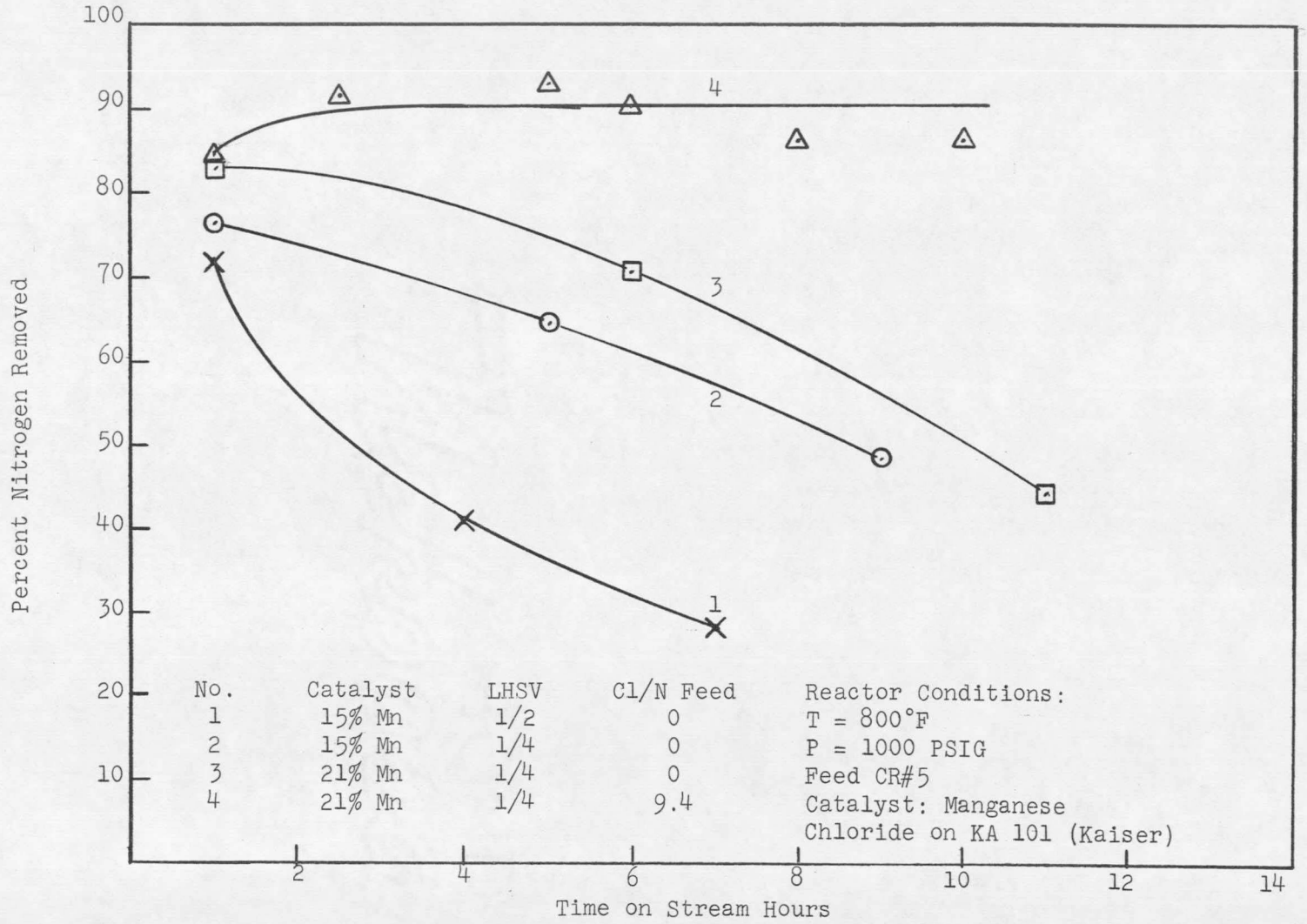


FIGURE I. Initial Data on Chloride Catalysts

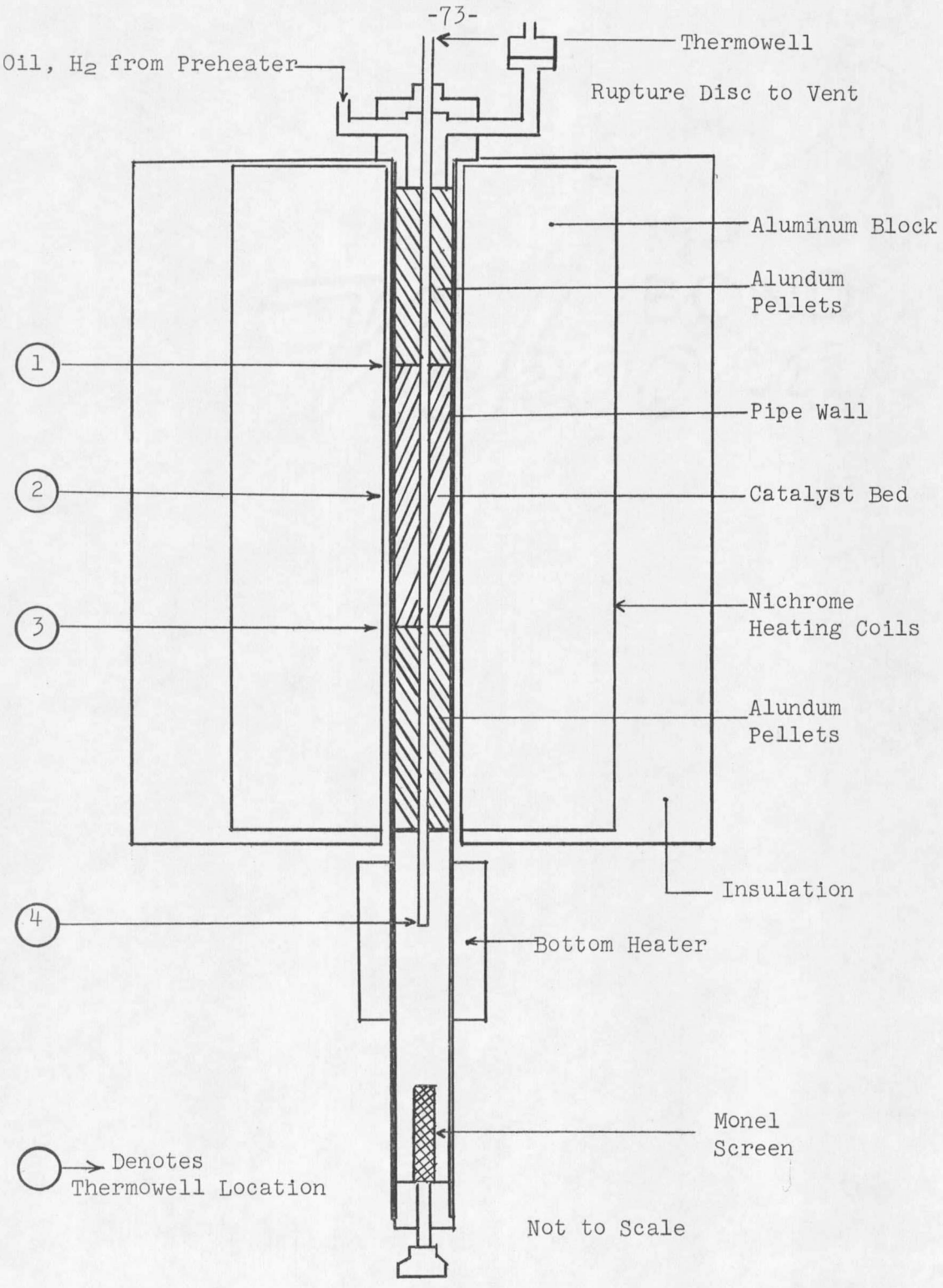


FIGURE 2. Detailed Diagram of Reactor

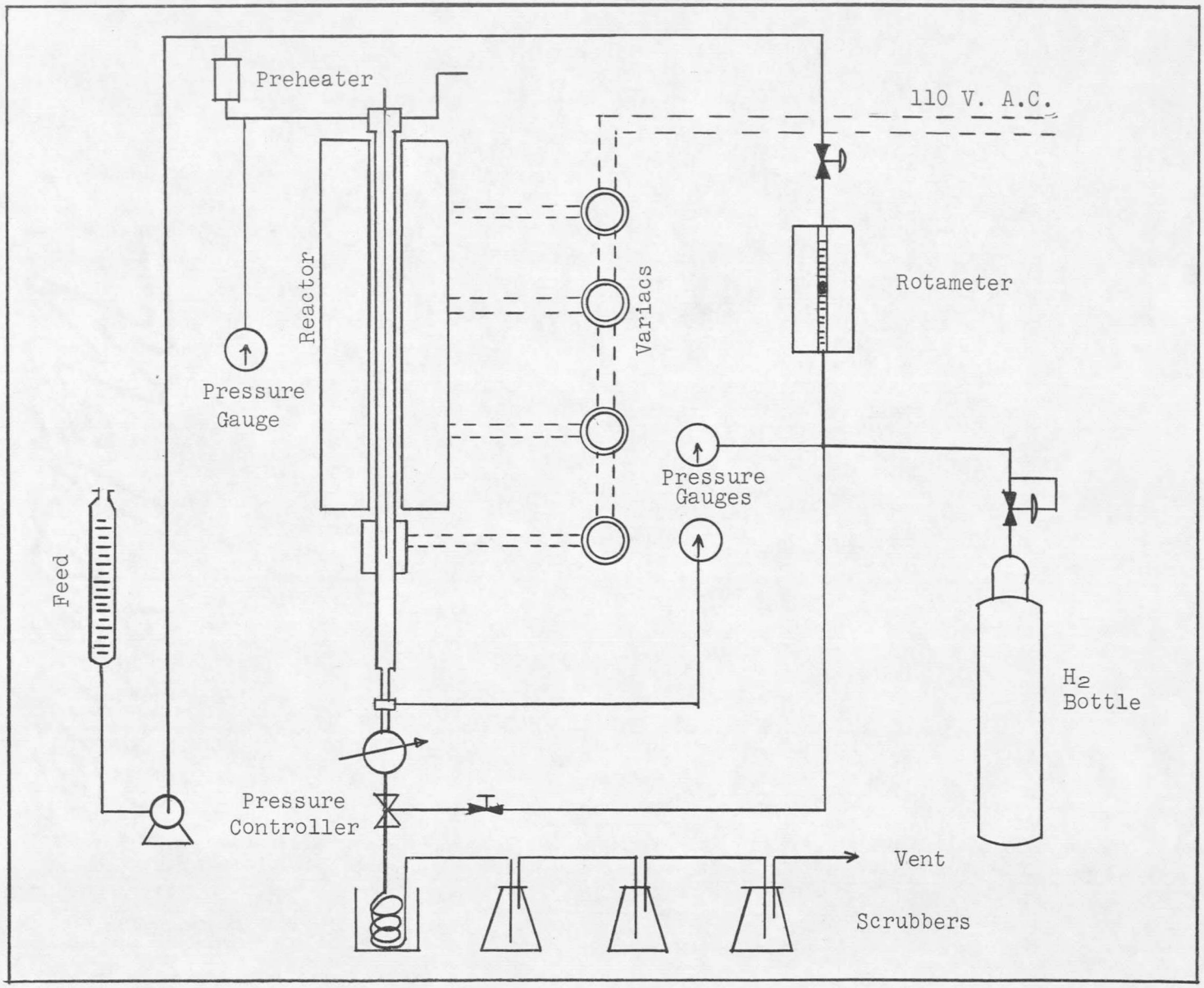


FIGURE 3. Schematic Flow Diagram of Reactor System

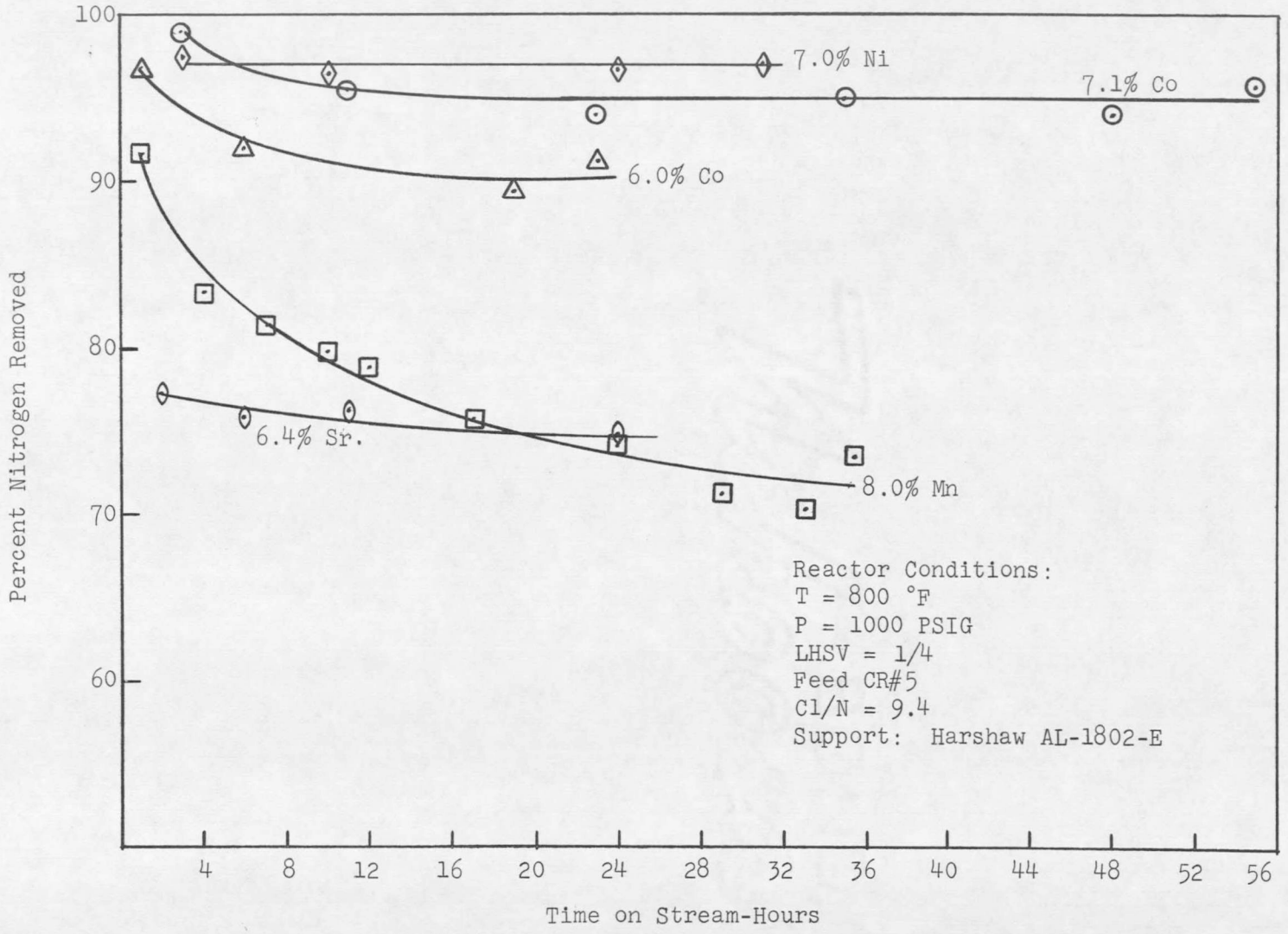


Figure 4. Comparison of Various Metal Chloride Catalysts

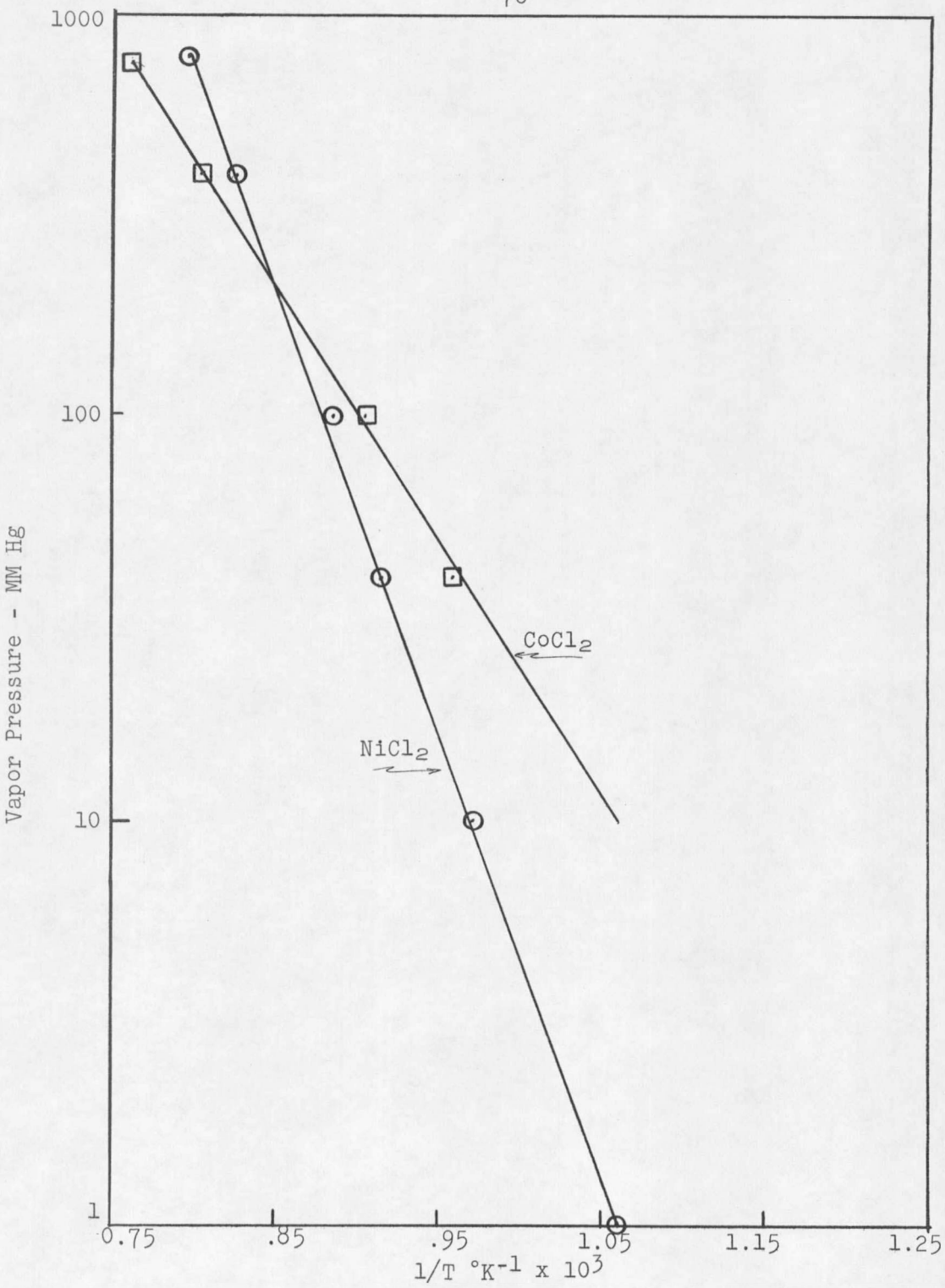


FIGURE 5. Vapor Pressure of $NiCl_2$ and $CoCl_2$

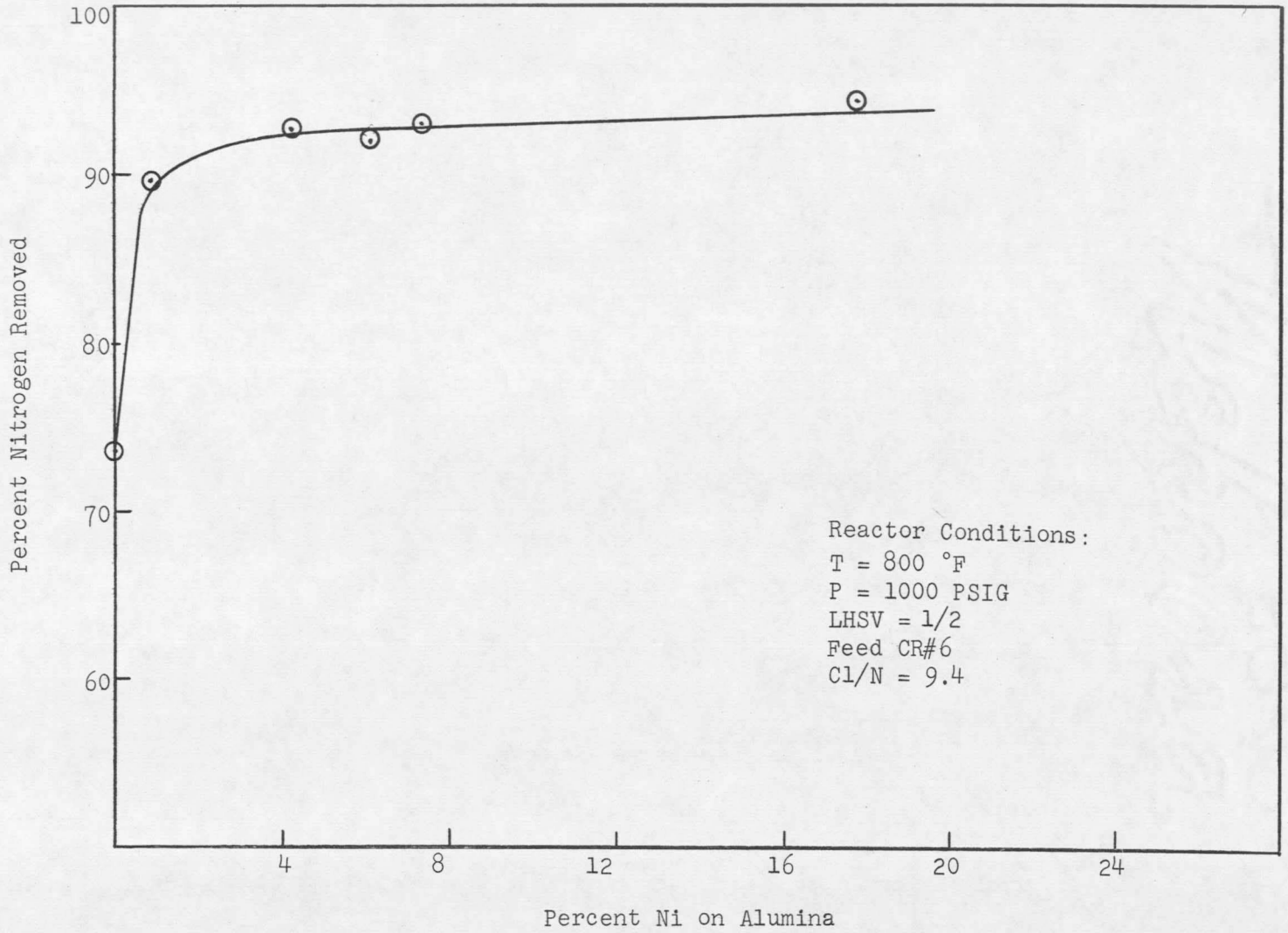


FIGURE 6. Nitrogen Removed as a Function of Nickel Content of Catalyst

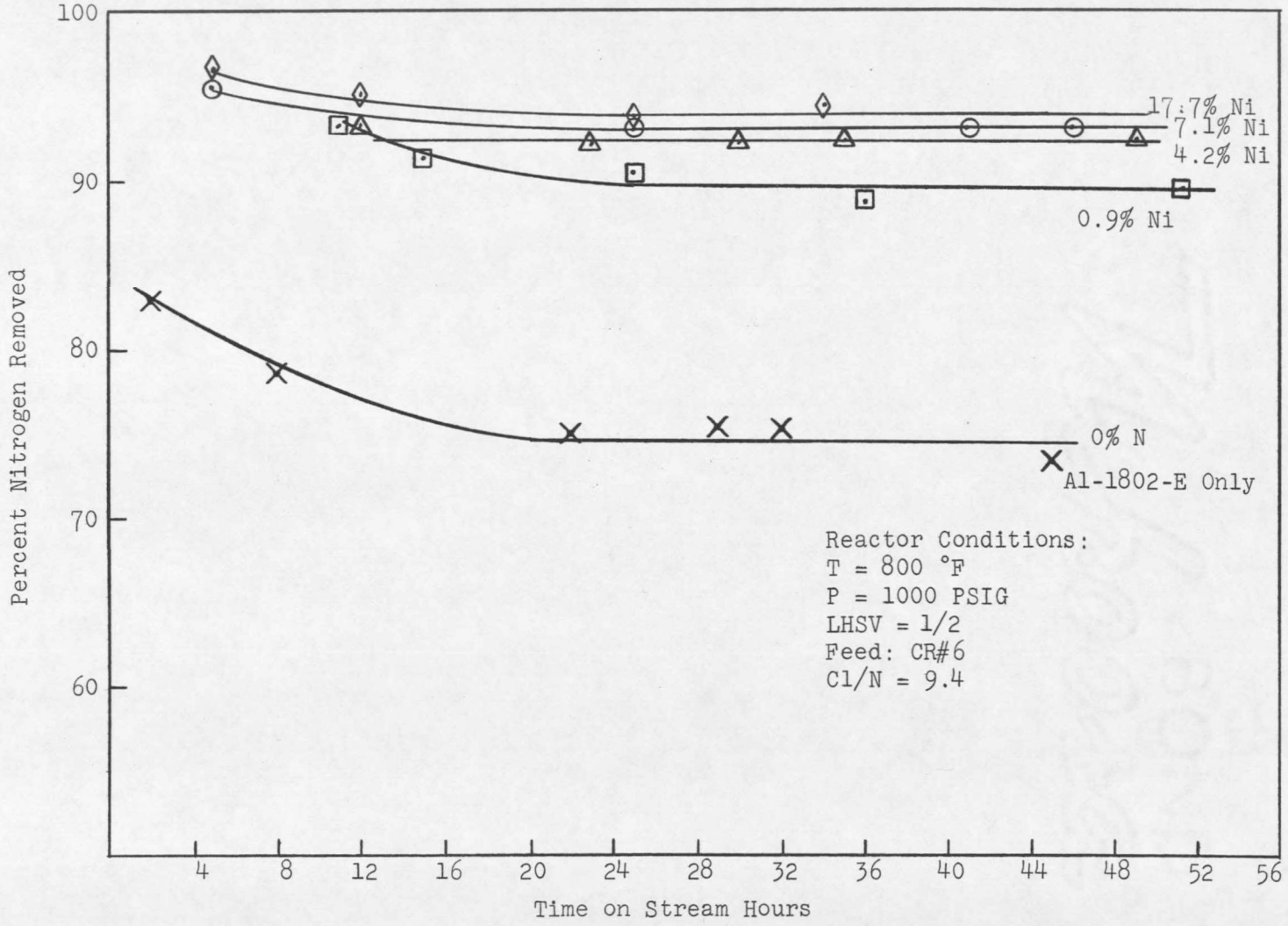


FIGURE 7. Nitrogen Removed as a Function of Time for Various Catalyst Compositions

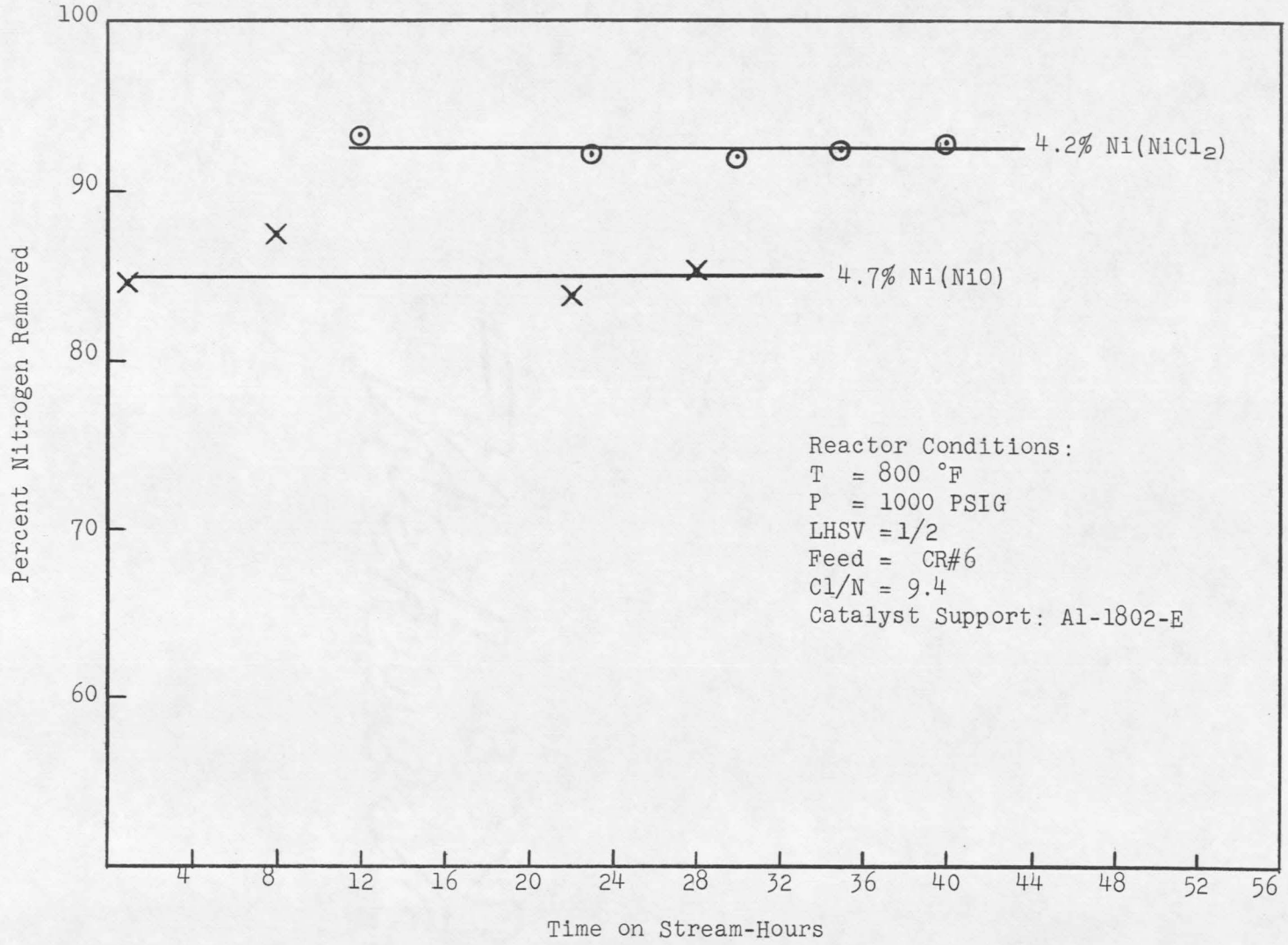


FIGURE 8. Comparison of $NiCl_2$ and NiO Catalysts. Nitrogen Removed as a Function of Time

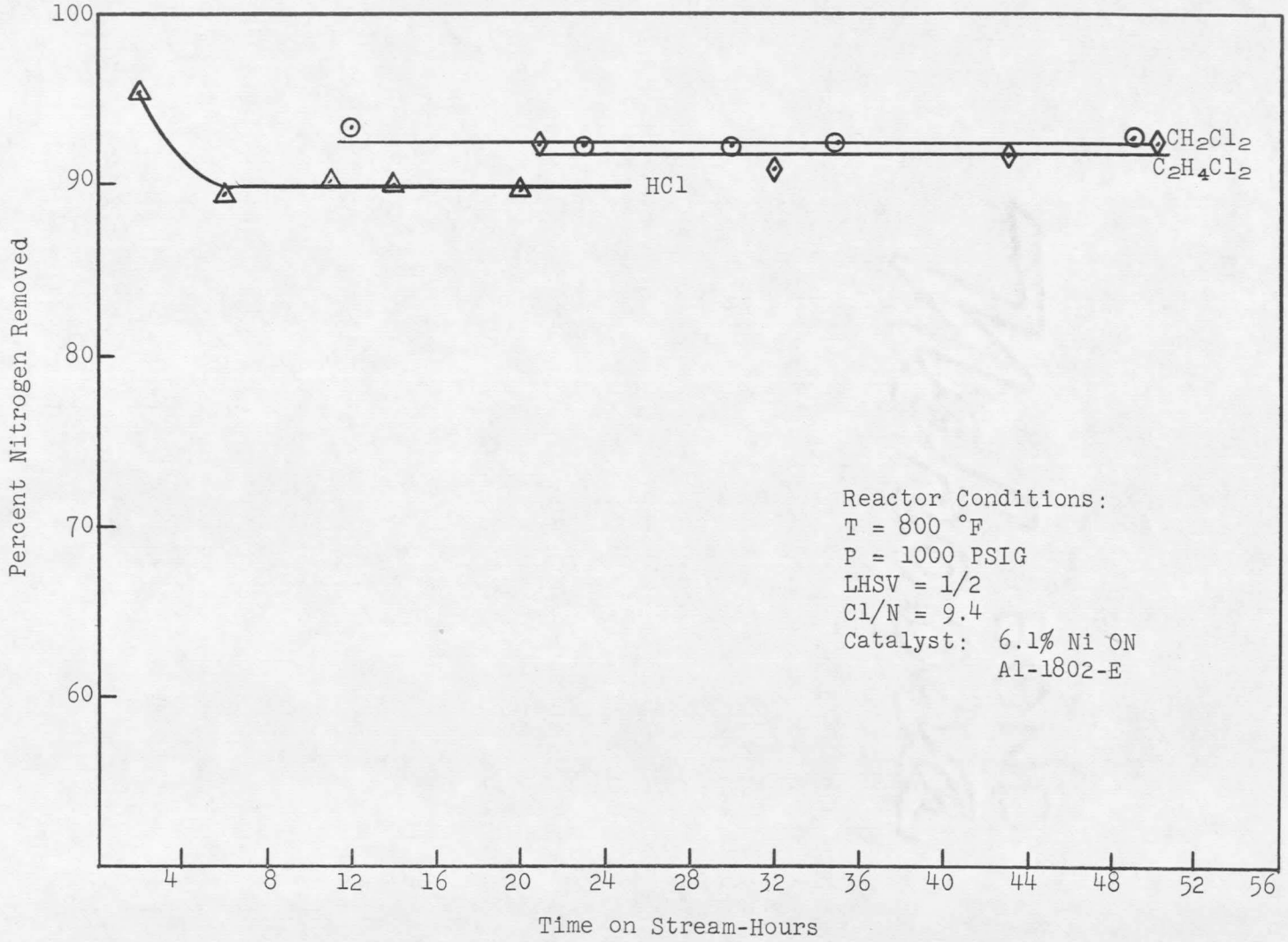


FIGURE 9. Comparison of Catalyst Activity Using Various Chlorides

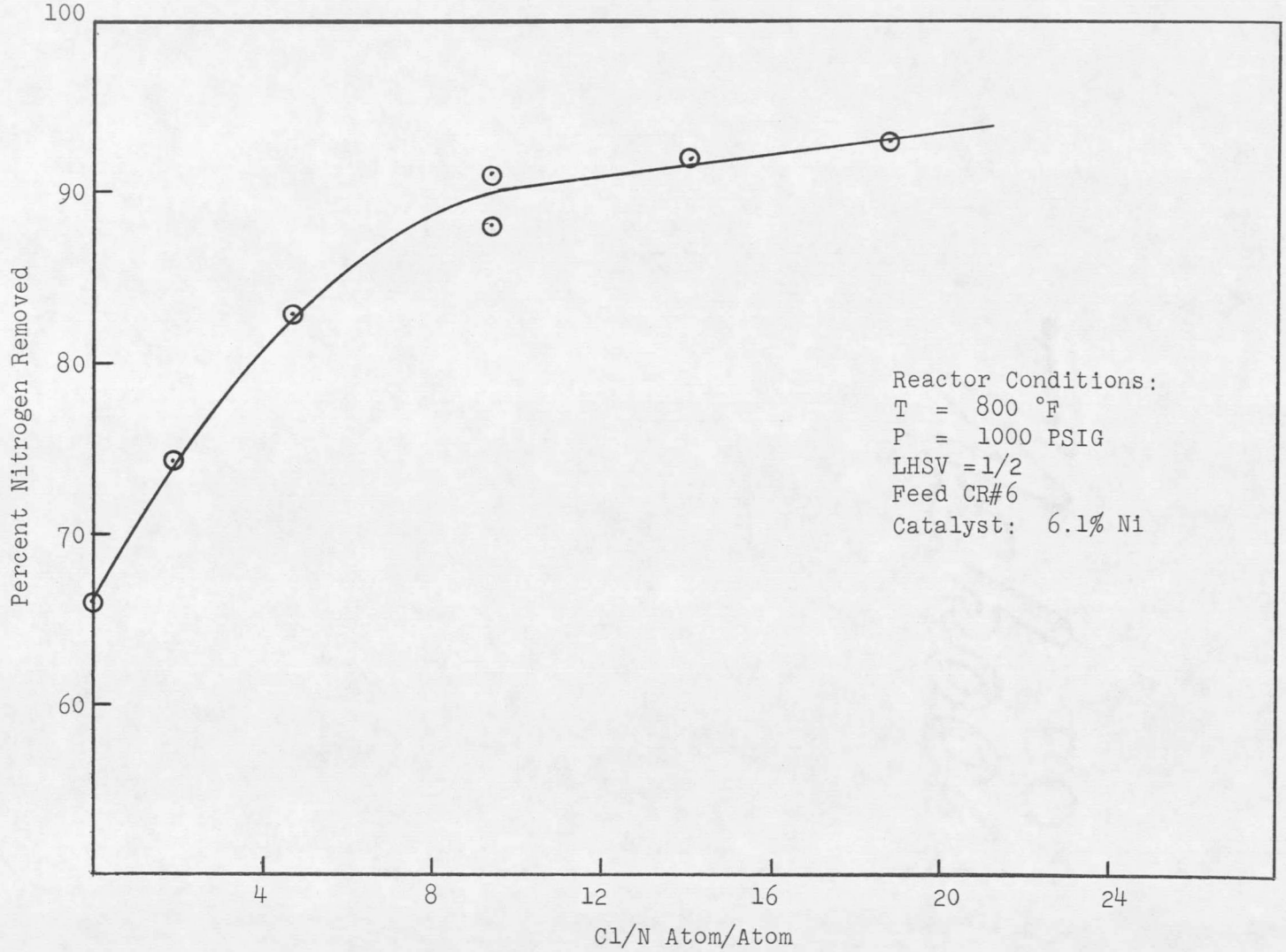


FIGURE 10. Nitrogen Removed as a Function of Cl/N Fed to Reactor

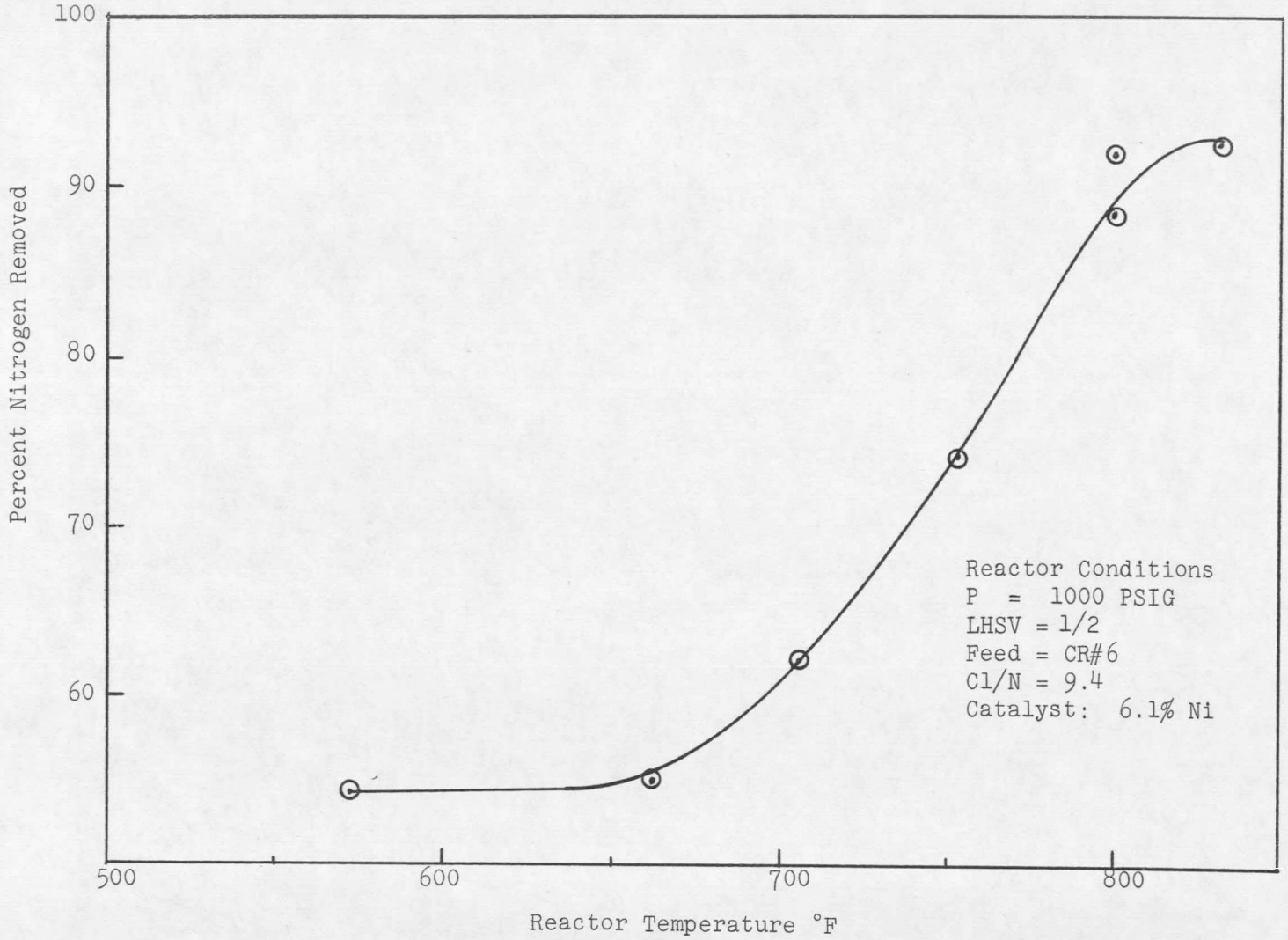


FIGURE 11. Nitrogen Removed as a Function of Reactor Temperature

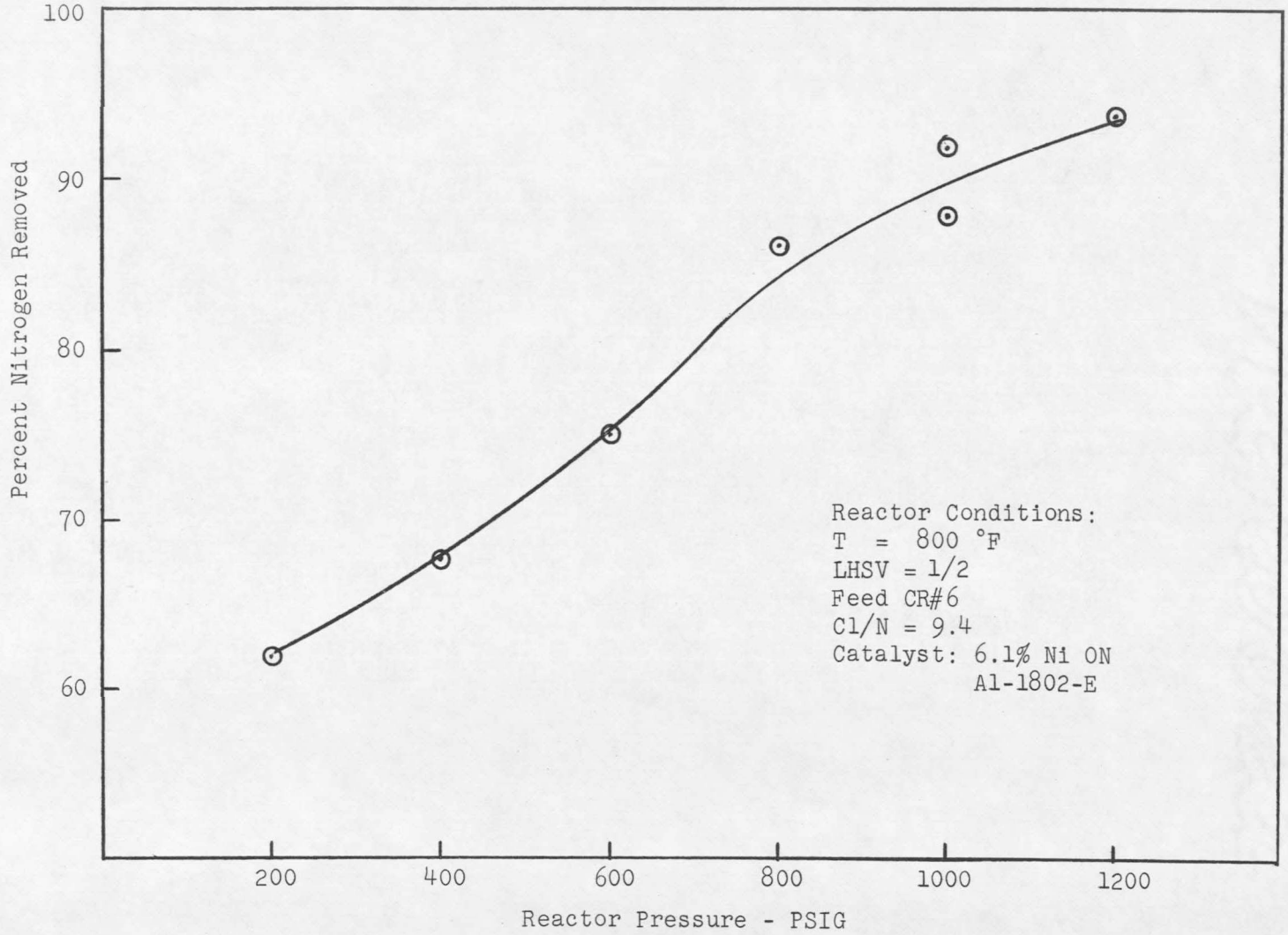


FIGURE 12. Nitrogen Removed as a Function of Reactor Pressure

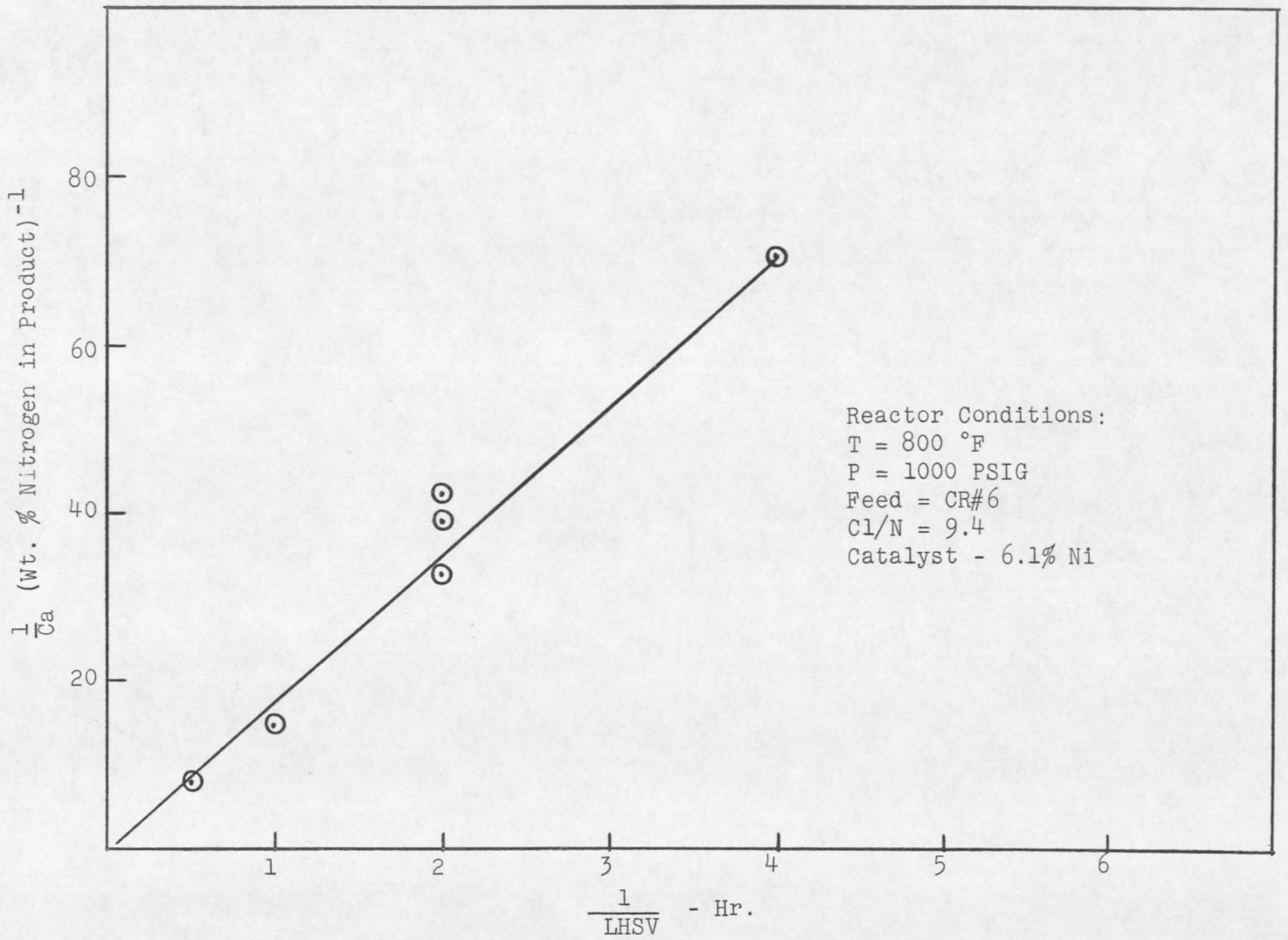


FIGURE 13. Test for Pseudo-Second Order Reaction for Hydrodenitrogenation

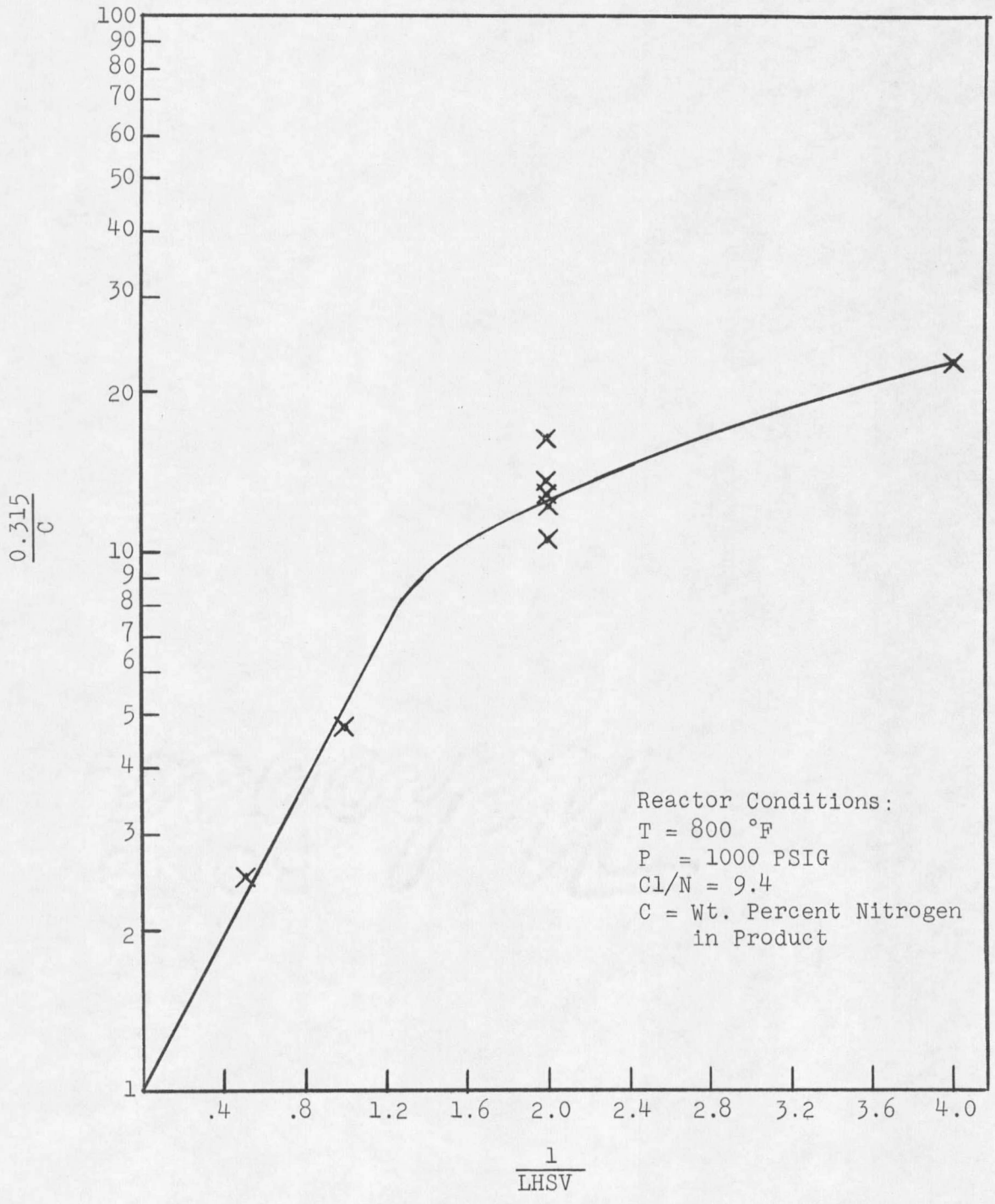


FIGURE 14. Test for Pseudo-First Order Reaction for Hydrodenitrogenation

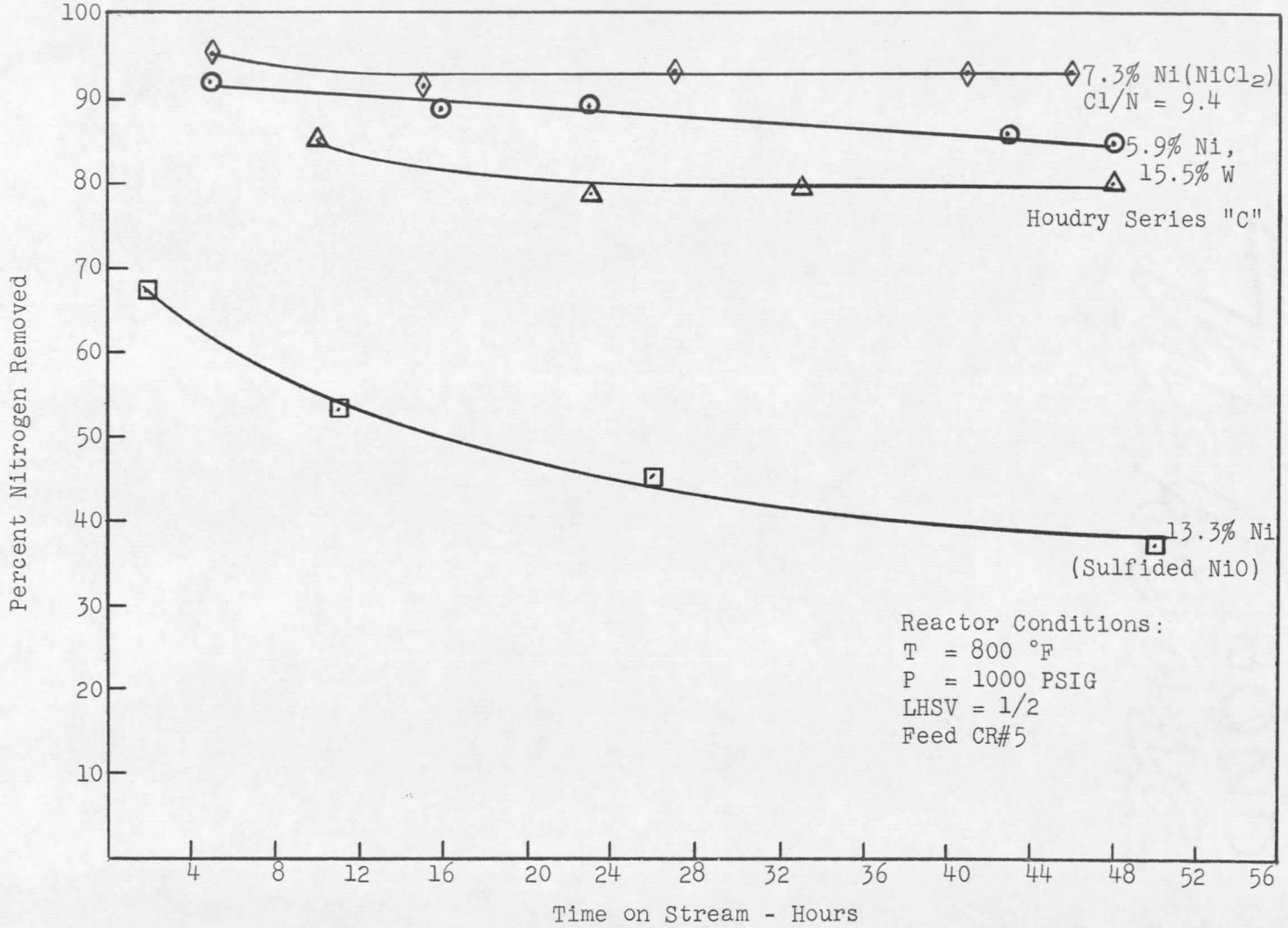


FIGURE 15. Comparison of $NiCl_2$-HCl System with Other Catalysts

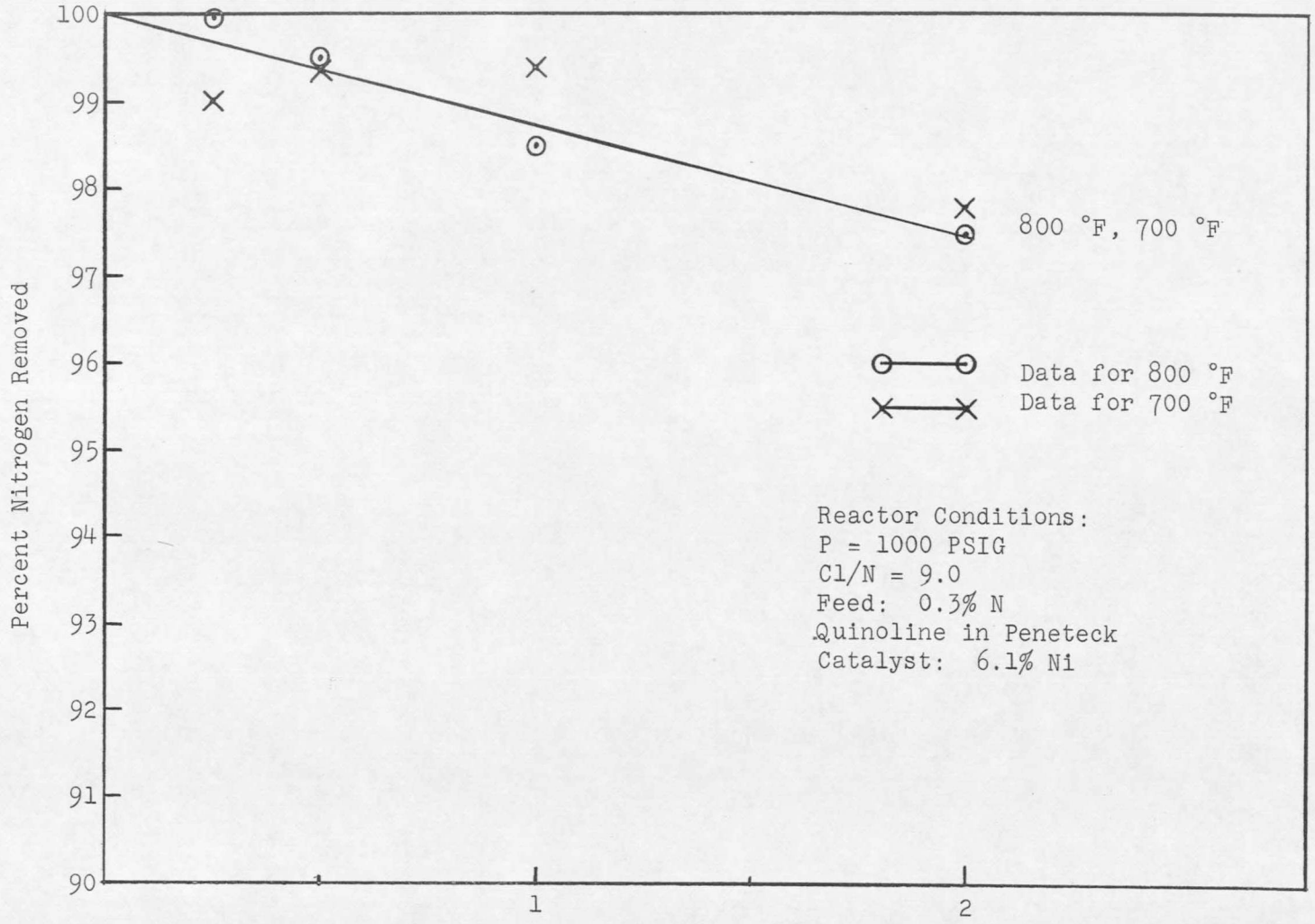


FIGURE 16. Nitrogen Removed as a Function of Space Velocity for Quinoline-Peneteck Mixture

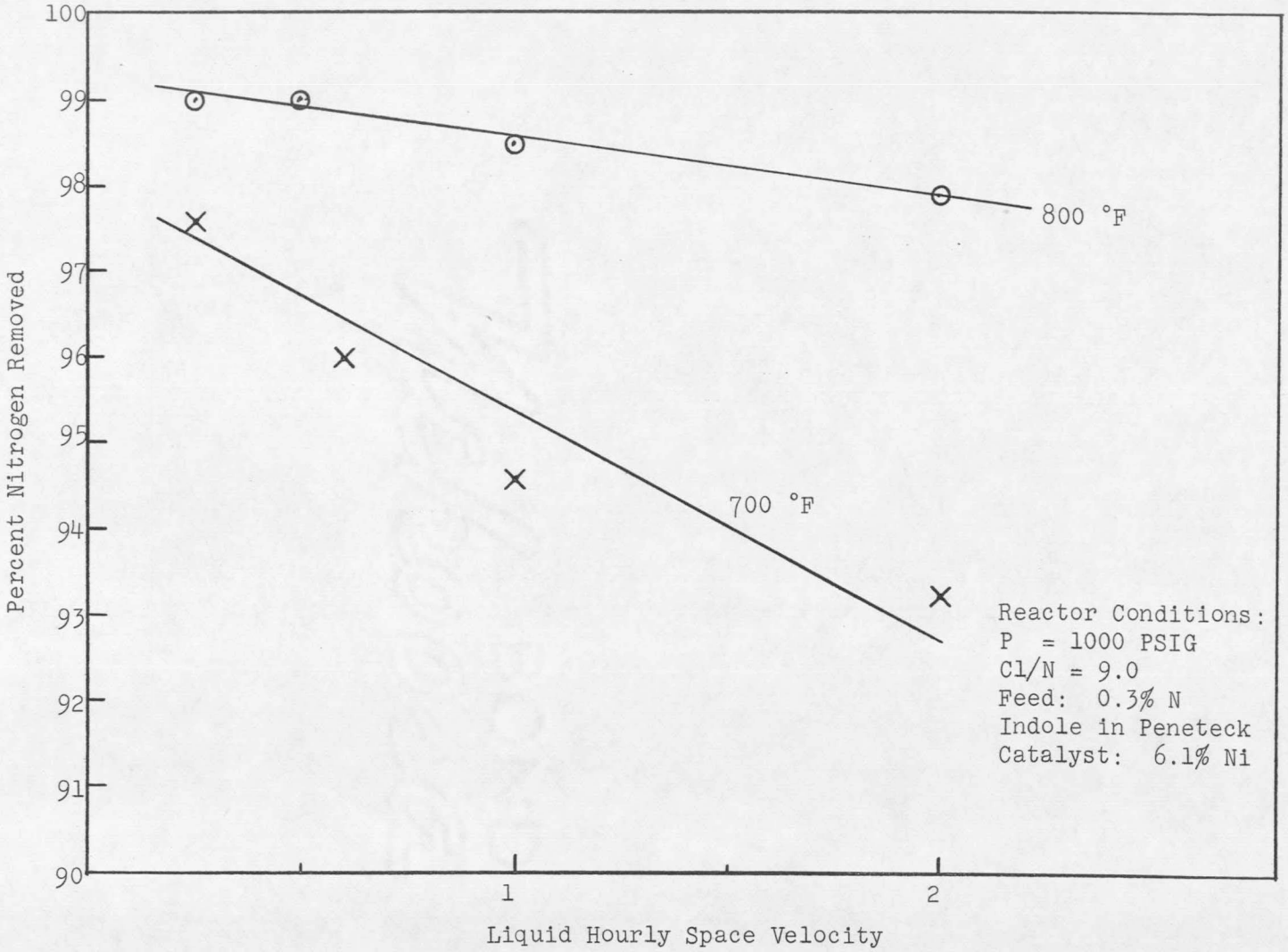


FIGURE 17. Nitrogen Removed as a Function of Space Velocity for Indole-Peneteck Mixture

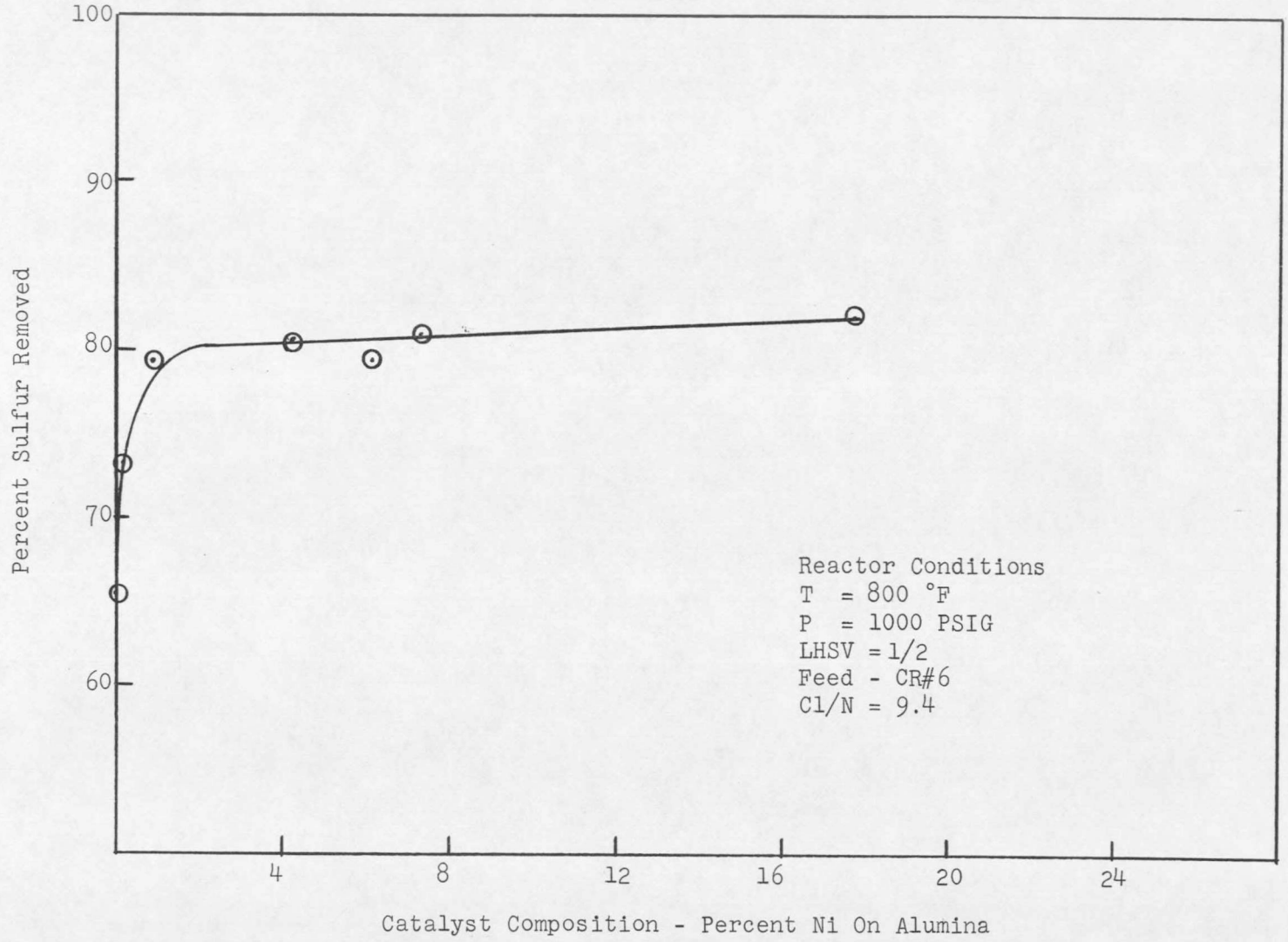


FIGURE 18. Sulfur Removed as a Function of Nickel Content of Catalyst

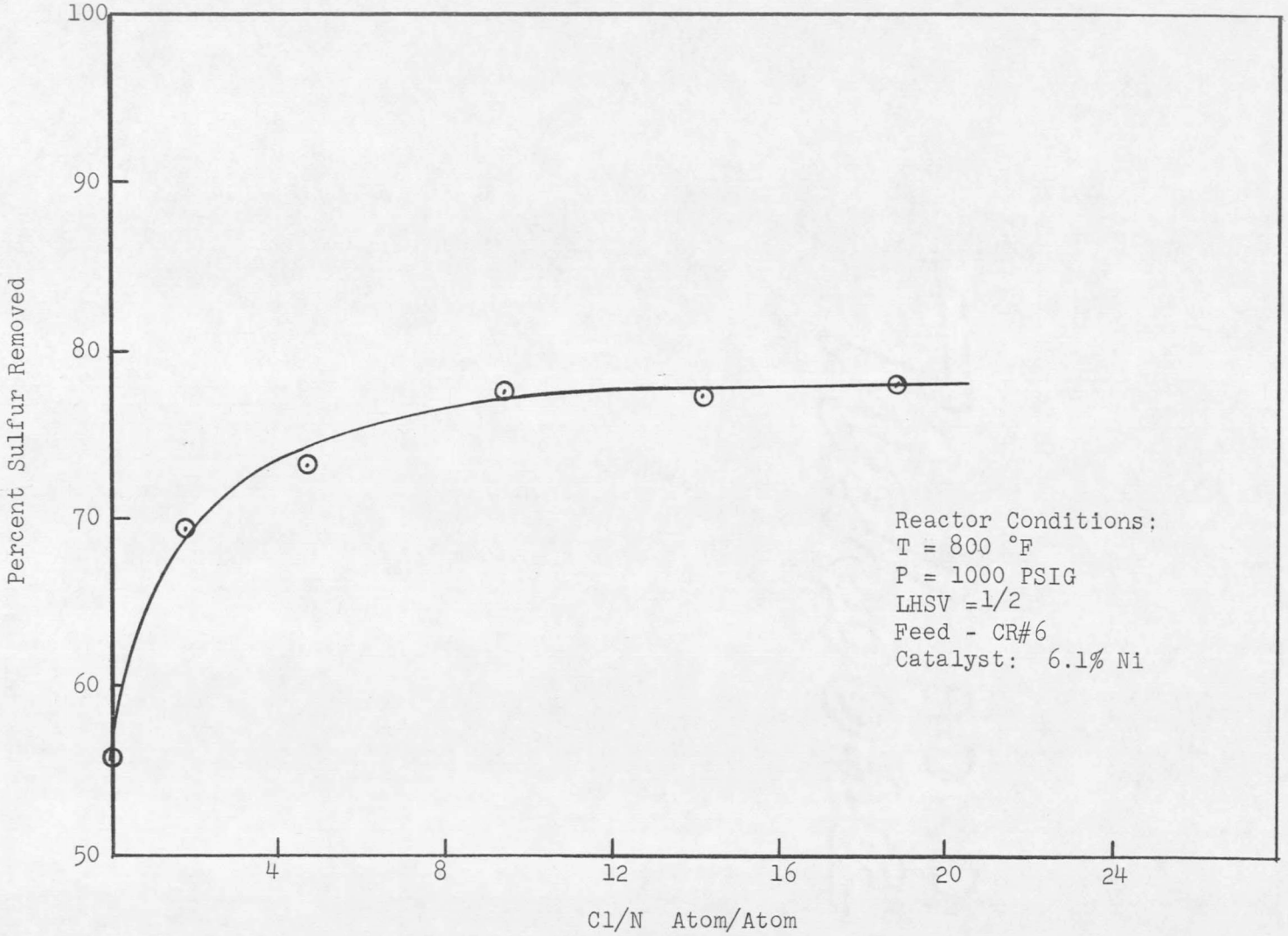


FIGURE 19. Sulfur Removed as a Function of Cl/N Fed to Reactor

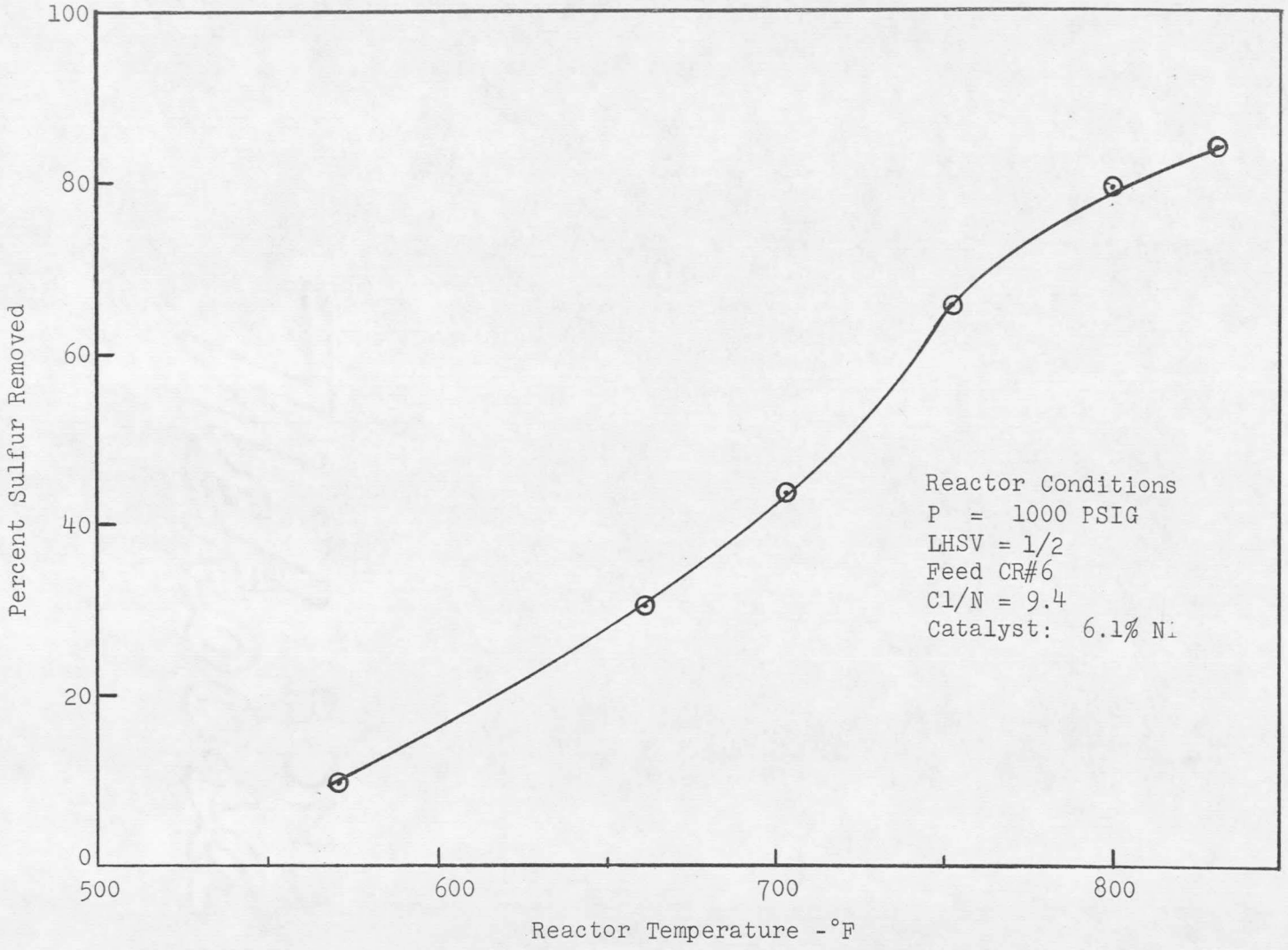


FIGURE 20. Sulfur Removed as a Function of Reactor Temperature

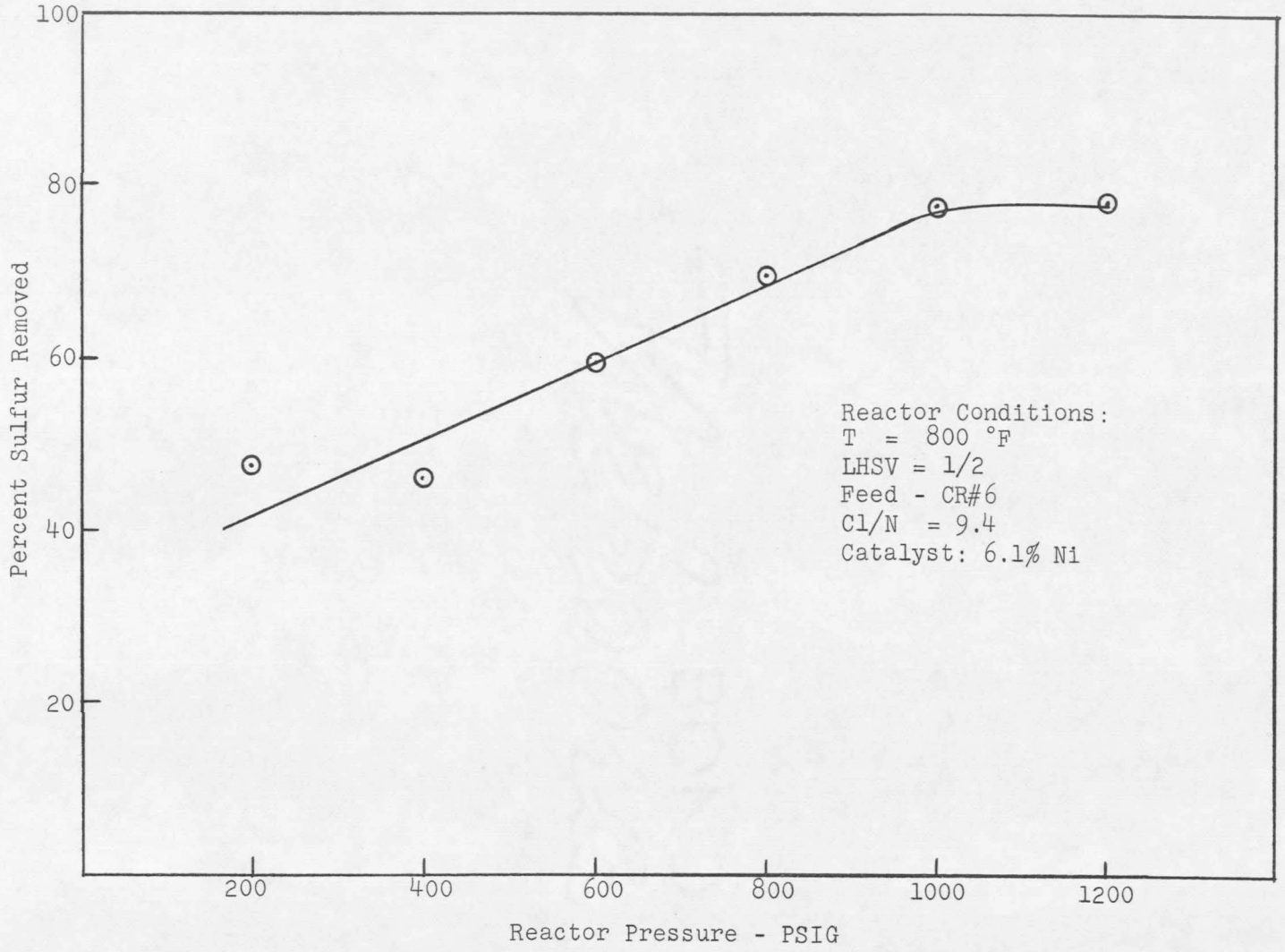


FIGURE 21. Sulfur Removed as a Function of Reactor Pressure.

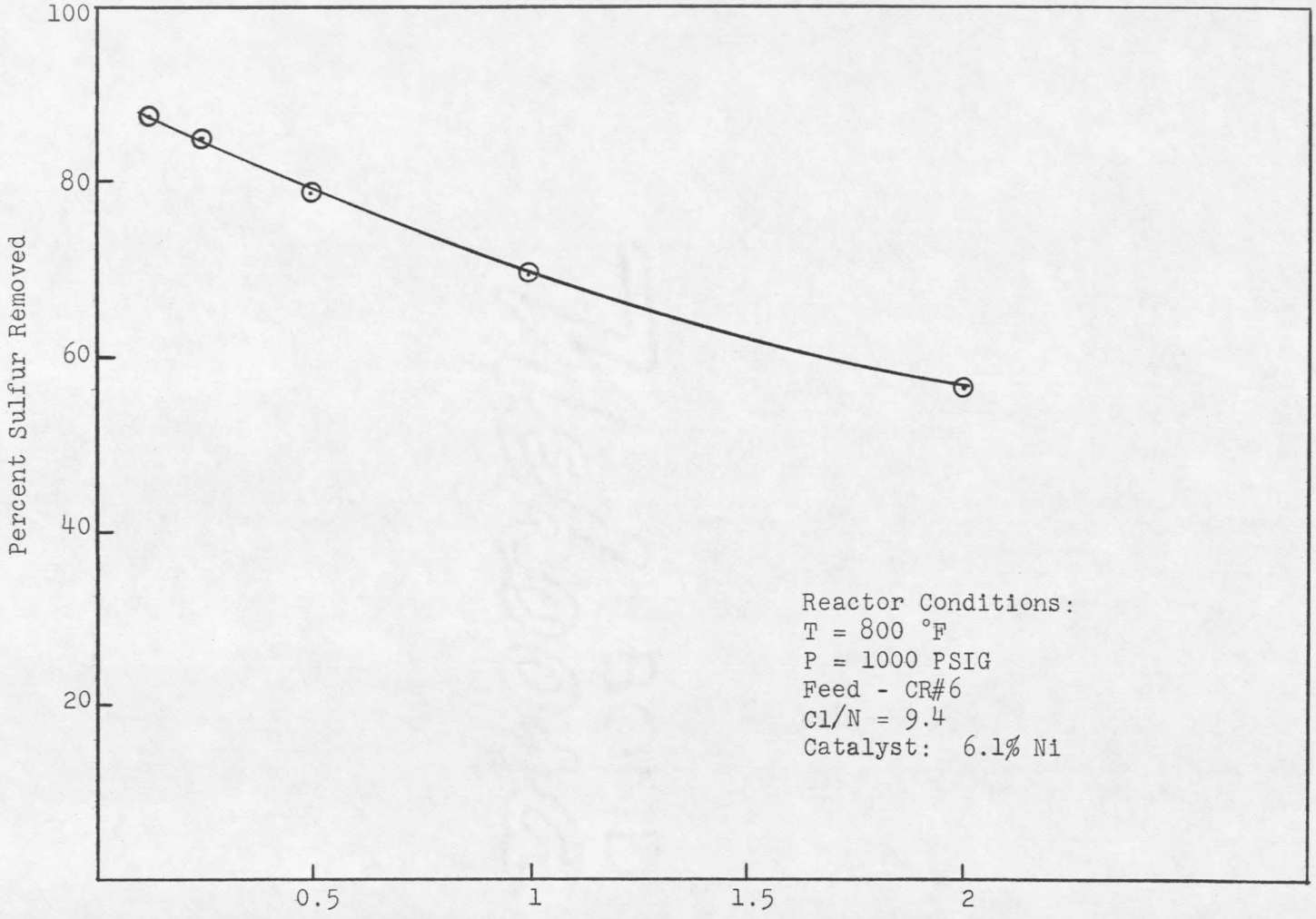


FIGURE 22. Sulfur Removed as a Function of Space Velocity

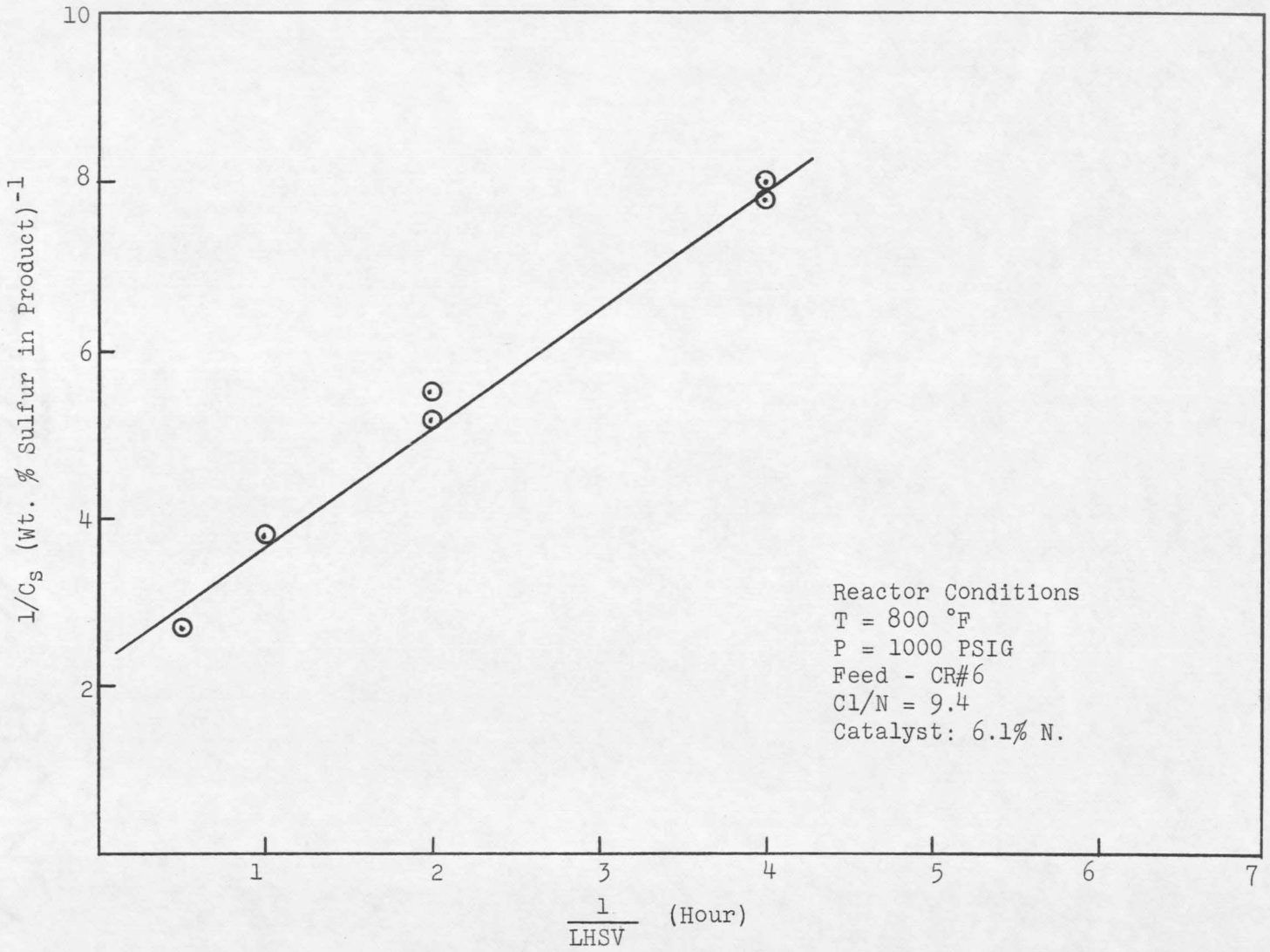


FIGURE 23. Test for Pseudo-Second Order Reaction for Sulfur Removal

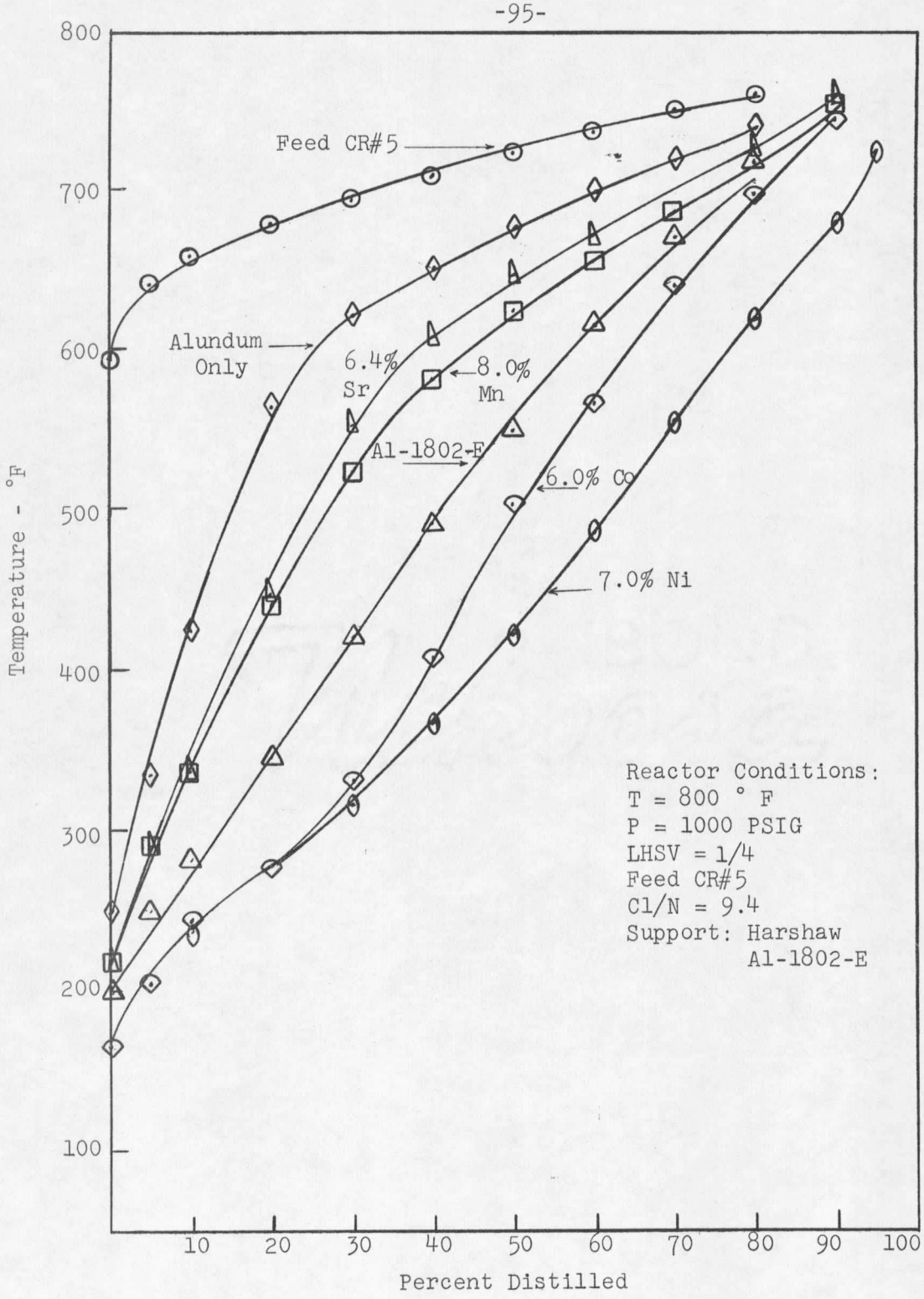


FIGURE 24. Preliminary Data on Cracking. ASTM D-158 Product Distribution for Various Metal Chloride Catalysts

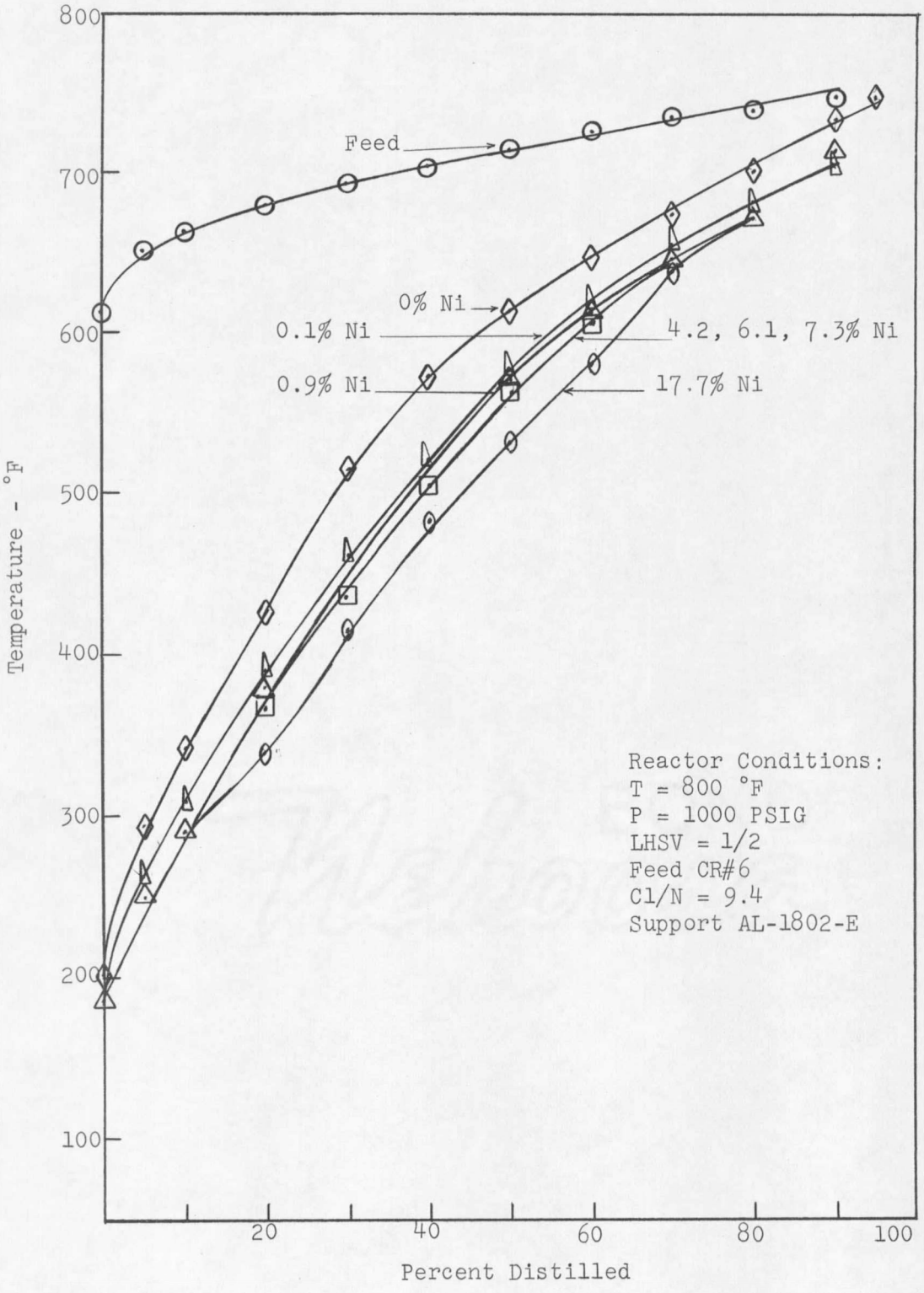


FIGURE 25. ASTM D-158. Effect of Catalyst Composition on Distribution of Product Oil.

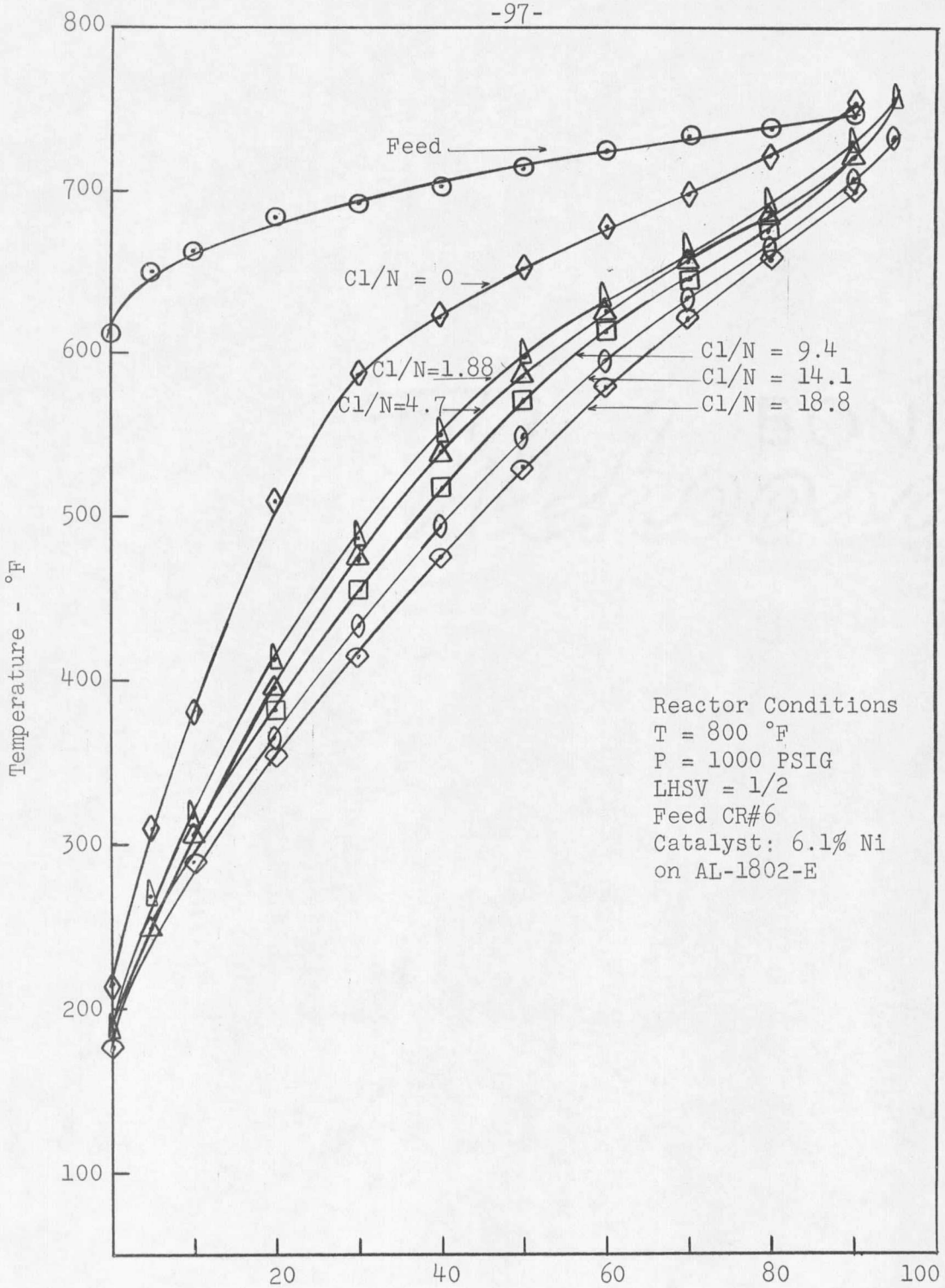


Figure 26. ASTM D-158. Effect of Cl/N Ratio on Distribution of Product Oil

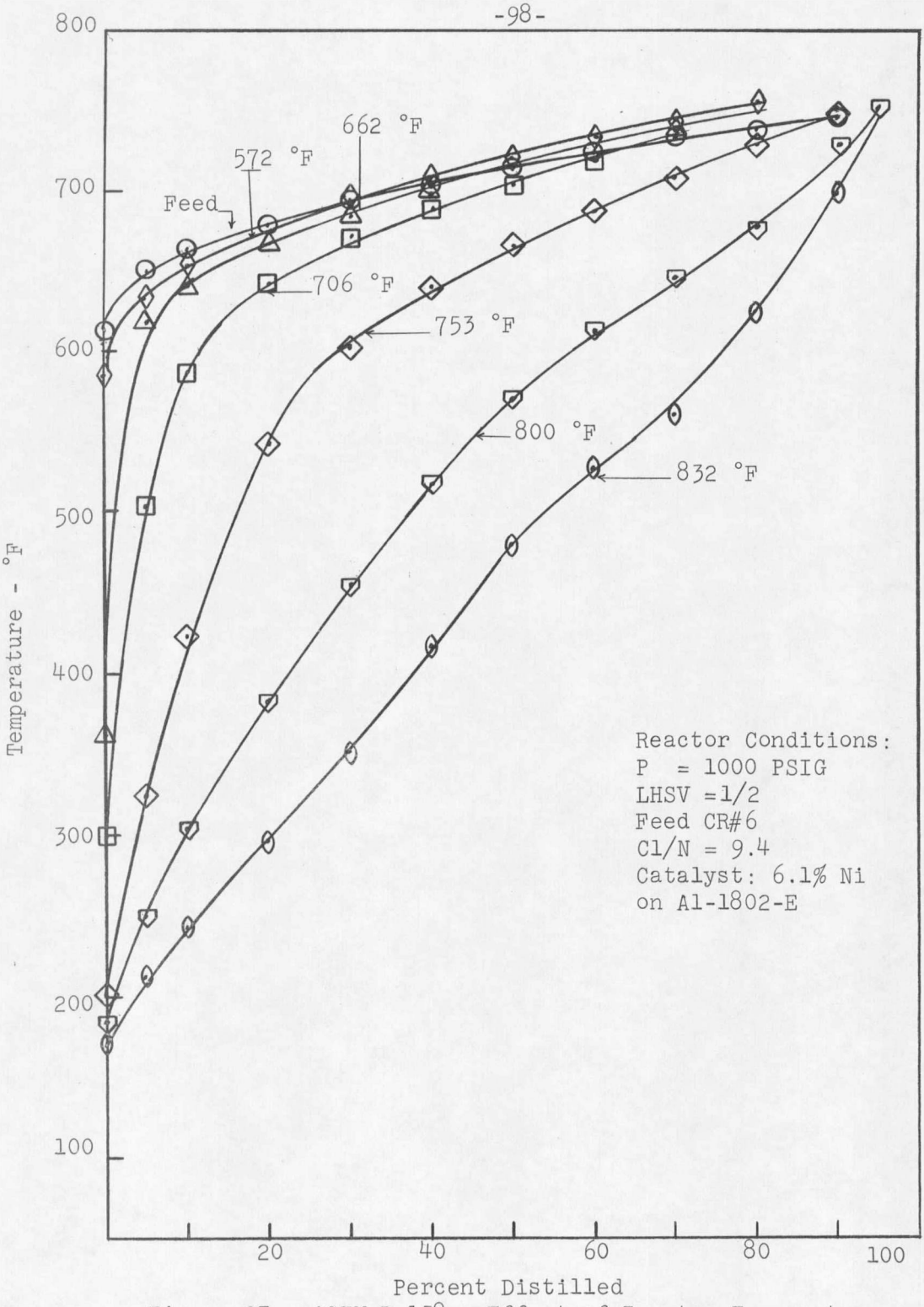


Figure 27. ASTM D-158. Effect of Reactor Temperature on Distribution of Product Oil

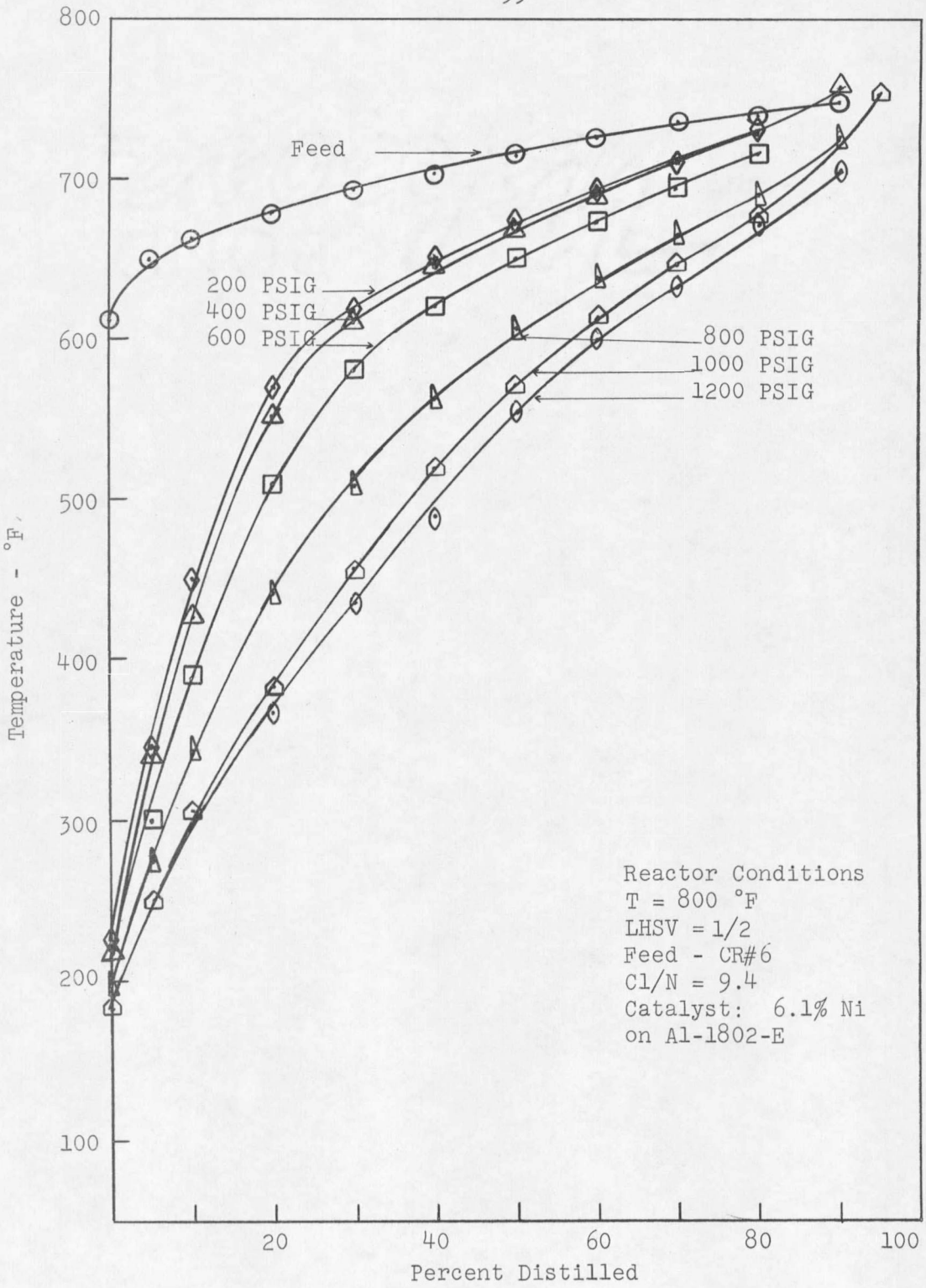


FIGURE 28. ASTM - D-158. Effect of Reactor Pressure on Distribution of Product Oil.

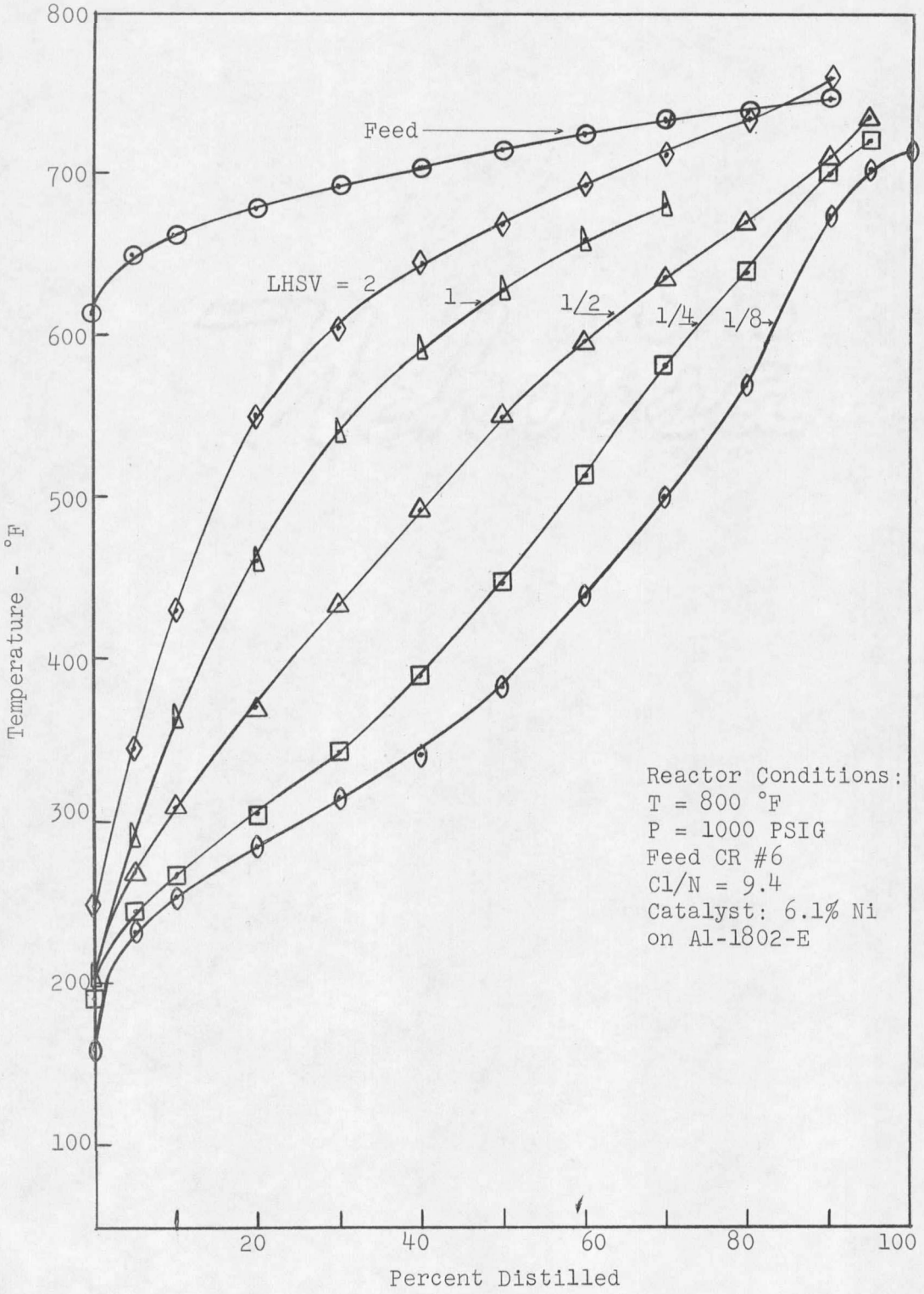


FIGURE 29. ASTM D-158. Effect of Space Velocity on Distribution of Product Oil

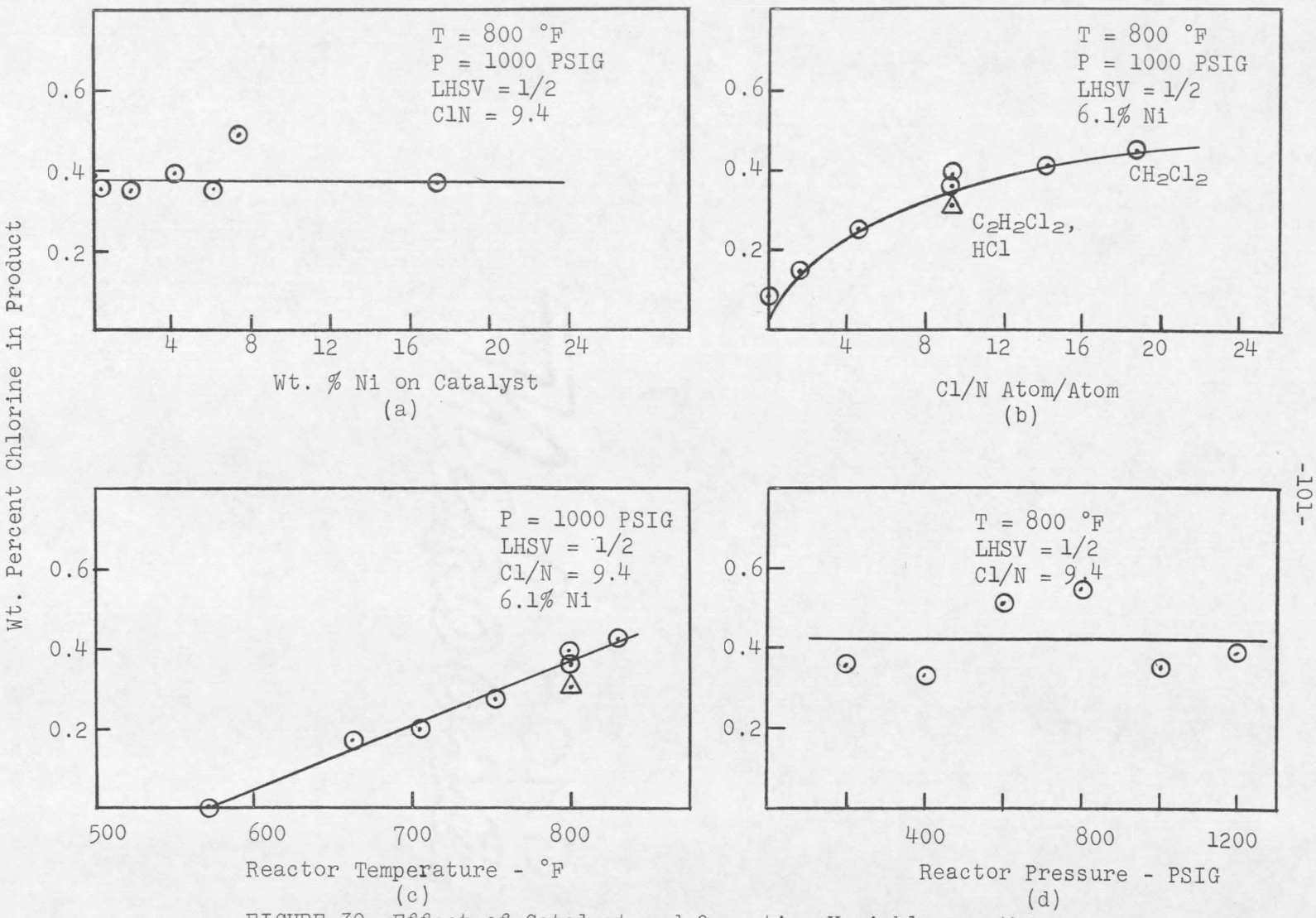


FIGURE 30. Effect of Catalyst and Operating Variables on the Amount of Chlorine in Oil Product

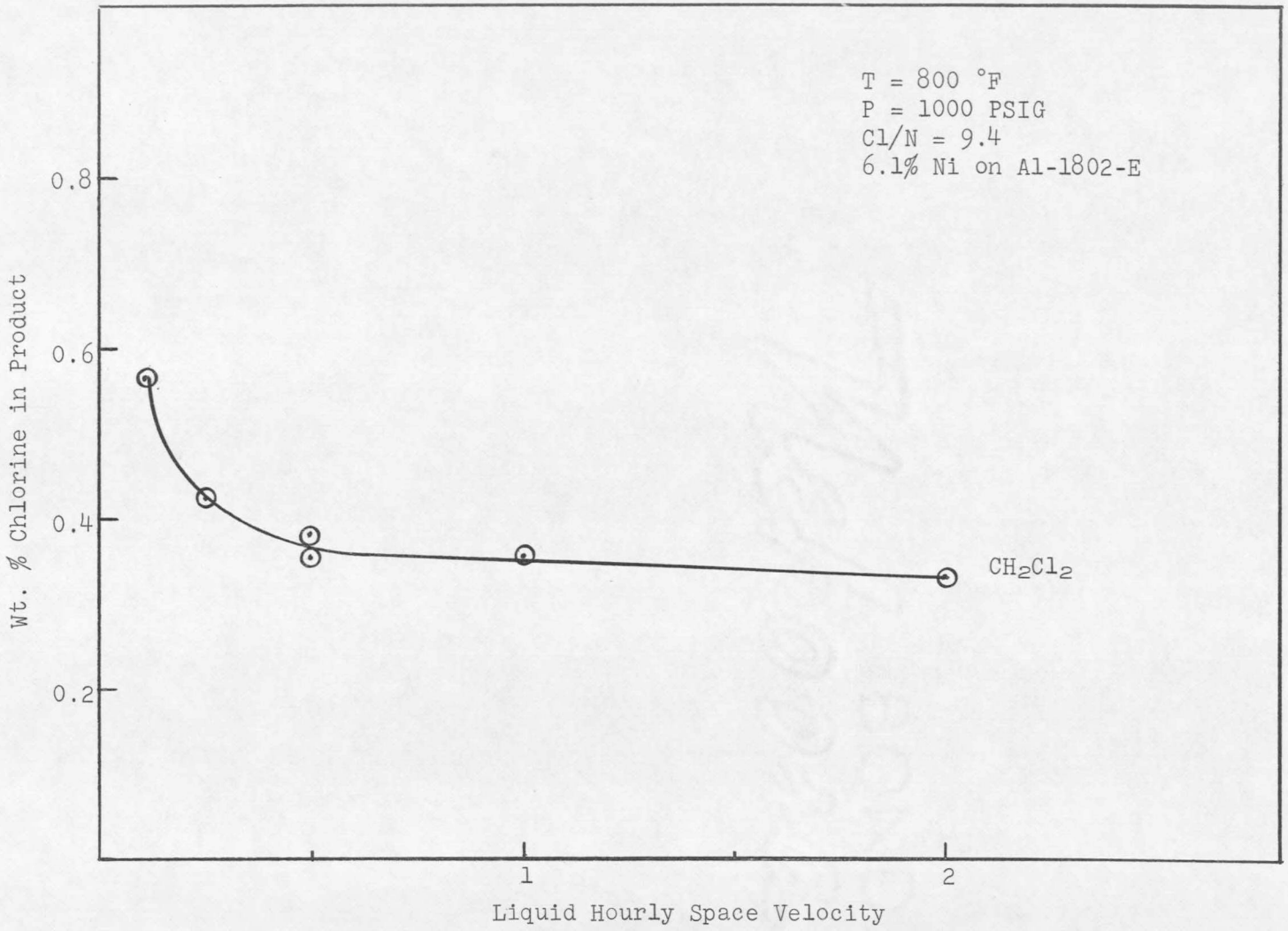


FIGURE 31. Effect of Space Velocity on the Amount of Chlorine in Oil Product

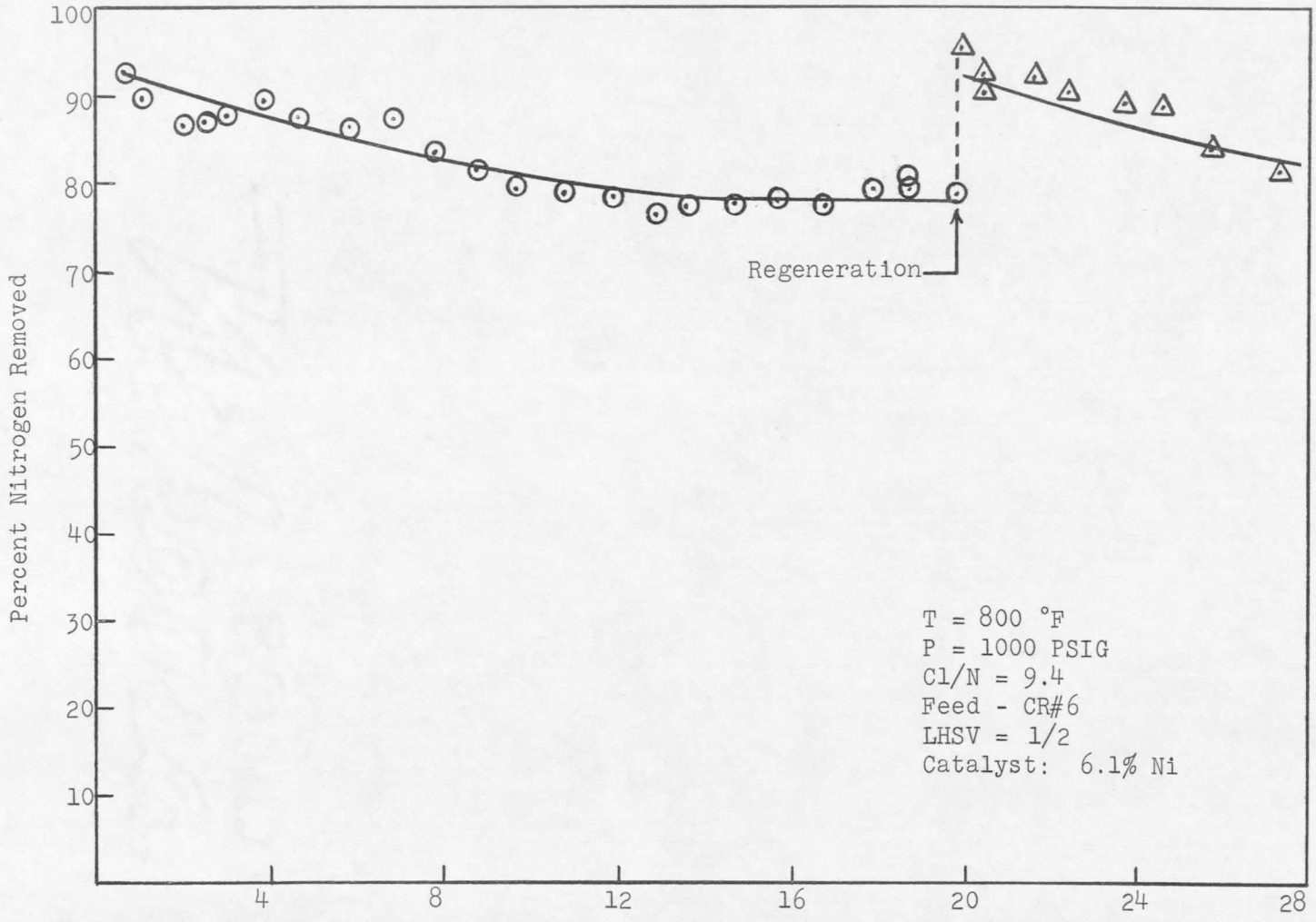


FIGURE 32. Nitrogen Removed as a Function of Time for an Extended Run

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