The catalytic hydrogenation of certain aliphatic amines
by Robert A Currie

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering
Montana State University
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Abstract:
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aliphatic amines were studied. The feed concentration and hydrogen rate were held constant for all
runs. The compounds studied were n-butyl amine, octyl amine, iso-butyl amine, sec-butyl amine, and
tert-butyl amine. An increase of temperature caused a corresponding increase in the conversion of the
nitrogen compound. An increase in pressure also caused an increase in the nitrogen conversion.

By comparing n-butyl amine to octyl amine, it was evident that the lower molecular weight amine
denitrogenated more readily. Similarly, the isomers of butyl amine denitrogenated in the order n-butyl
amine, iso-butyl amine, sec-butyl amine and tert-butyl amine, with the ease-of denitrogenation
increasing respectively. The product formed from n-butyl amine is a mixture of iso-butane and
n-butane. Sec-butyl amine forms essentially n-butane, while iso- and tert-butyl amine form essentially
iso-butane at high conversions.
THE CATALYTIC HYDROGENATION
OF CERTAIN ALIPHATIC AMINES

by

ROBERT A. CURRIE

A THESIS
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The effects of pressure, temperature, and space velocity on the hydrodenitrogenation of certain aliphatic amines were studied. The feed concentration and hydrogen rate were held constant for all runs. The compounds studied were n-butyl amine, octyl amine, iso-butyl amine, sec-butyl amine, and tert-butyl amine.

An increase of temperature caused a corresponding increase in the conversion of the nitrogen compound. An increase in pressure also caused an increase in the nitrogen conversion.

By comparing n-butyl amine to octyl amine, it was evident that the lower molecular weight amine denitrogenated more readily. Similarly, the isomers of butyl amine denitrogenated in the order n-butyl amine, iso-butyl amine, sec-butyl amine and tert-butyl amine, with the ease of denitrogenation increasing respectively. The product formed from n-butyl amine is a mixture of iso-butane and n-butane. Sec-butyl amine forms essentially n-butane, while iso- and tert-butyl amine form essentially iso-butane at high conversions.
I. INTRODUCTION

When a nation's industrial picture is changing rapidly, new processes and products must be introduced at a corresponding rate. But with each new or improved process, more demands are placed on each intermediate step. These demands may be quite diversified, but one of the largest demands falls on the specifications and requirements of an intermediate used. This rapidly changing industrial picture applies directly to most chemical and petroleum industries.

With any industrial changes or new growth, new markets are created. To supply these markets larger and different sources and raw materials and intermediates are needed. Often new sources of these materials must be used, which may require the use of inferior grades. This immediately presents the problem of upgrading the materials to meet the required specifications. Demands to improve any product present new problems that must be met and handled. If the information needed to obtain a complete knowledge of the problem is not available, then it may be necessary to conduct studies to obtain this information.

In recent years one problem has arisen that exemplifies this demand. This problem concerns itself with the efficient removal of nitrogen-containing compounds from the petroleum distillates of which they are a part.

Since 1953 the Esso Research and Engineering Company has sponsored a research project at Montana State College. Not only was this study
conducted here, but also in their own research laboratories. The purpose of the project was to study the removal of sulfur by hydrodesulfurization which also included in-cycle catalyst deactivation studies (6, 9, 11, 16). Recently, however, the study has been carried to the level where it is no longer desirable to continue this type of work at the present time. Since 1959 and the completion of Mahugh's thesis, attention has been focused on hydrodenitrogenation. Because of previous experience with desulfurization and the similarities between this and denitrogenation, this new study was conducted in much the same way as desulfurization.

In an effort to understand better a small portion of the overall problem, this study was conducted on only one type of nitrogen compound. The type of nitrogen compound used in this study was limited to aliphatic amines. However, this type of compound makes up a part of the total nitrogen content of many commercial petroleum feedstocks. The effects upon hydrogenation of such variables as pressure, temperature, space velocity, and structure of the amines were studied, and their correlations to hydrogenation were examined.

The feedstock used in this study was blended to resemble some of the characteristics of a commercial feed. However, only one type of nitrogen compound of known concentration was introduced into the feed. This made it possible to understand better the
behavior of this compound to hydrogenation.

Commercial feeds may contain several types of nitrogen compounds. Some of the more common compounds encountered are as follows:

1. \( \text{R} - \text{C} - \text{NH}_2 \)  
   \( \text{H} \)  
   Amines

2. \begin{center} ![Quinoline](image) \end{center}  
   Quinoline

3. \begin{center} ![Isoquinoline](image) \end{center}  
   Isoquinoline

4. \begin{center} ![Pyridine](image) \end{center}  
   Pyridine

5. \begin{center} ![Pyrrole](image) \end{center}  
   Pyrrole

6. Figurations undetermined  
   Porphyrins

A feedstock may contain many more types of nitrogen compounds than these. Also, each type of compound may have more than one possible arrangement of atoms in its structure. As an example, quinoline differs from isoquinoline in only the placement of the nitrogen atom in the heterocyclic ring. Since many compounds are present in most feedstocks, numerous reactions may occur simultaneously. Some of the problems encountered in hydrogenation are as follows:
1. Does the presence of different nitrogen compounds cause an interaction that would affect the hydrogenation?

2. Does the presence of compounds other than nitrogen-containing compounds affect hydrogenation?

3. What affect does the carrier have on hydrogenation?

4. What part of the reaction is rate controlling?

5. What physical conditions and limits are present?

6. How do variables like pressure and temperature affect the hydrogenation?

In most cases before a study like this is conducted, there must first be sufficient interest to merit such an investigation. Reasons leading up to the desire to remove nitrogen compounds are numerous and diversified. Some of the more obvious reasons are as follows:

1. When nitrogen-containing compounds come into contact with sensitive catalysts, the catalysts are easily poisoned and quickly lose their efficiency. Some processes in which this may occur are catalytic cracking, hydrogen platforming, and alkylation (1, 10).

2. Nitrogen compounds are partially responsible for extensive gum formation. This formation is caused by their ability to accelerate the oxidation of numerous unsaturated compounds (15).
3. Removal of nitrogen compounds to produce a product that is competitive with those from other sources. The removal of nitrogen compounds from shale oil to upgrade its quality would be an example. The catalytic hydrogenation of crude shale oil has been studied by the Chemical Engineering Department at Montana State College since 1954 (2, 5, 7).

4. Nitrogen compounds are often the source of objectionable odors (15).

5. Nitrogen impurities can hinder various chemical processes. The purpose and reasons for this study have been previously stated. The information obtained from this study is of fundamental nature and should be of value in solving the broader problem of upgrading commercial feedstocks.
II EXPERIMENTAL CONSIDERATIONS

A. Introduction

Carrier: In order to prepare a feedstock that contained the desired amount of nitrogen as amines, it was necessary to use a hydrocarbon carrier that simulated commercial feedstock characteristics. It was necessary to choose a carrier that in barrel lots was reasonably priced, that would blend readily with various low molecular weight amines, and not affect the hydrogenation process itself.

The hydrocarbon carrier chosen was normal heptane, which has a boiling point of 98.5°C and a density of 0.6838 gm/cc (4). The normal heptane was purchased in barrel lots from the Phillips Petroleum Company.

Process Conditions: The operating conditions chosen for this study were originally selected with the assistance of the Esso Research and Engineering Company. After a few exploratory runs were conducted, the conditions were modified to prevent total nitrogen conversion and also to be more compatible with the limitations of the equipment involved and the analytical techniques used. The following conditions were finally selected:

Pressure - 100 - 500 psig.
Temperature - 625°F - 725°F.
Hydrogen flow rate - 500 SCF/bbl.
Nitrogen concentration - 1.0% N by wt.
Space velocity - 10 - 100 gm/gm per hour.
B. Materials

**Feedstock:** The various amines used in this study were commercial grade reagents purchased from Eastman Organic Chemicals. The desired amine was blended with n-heptane to produce approximately 1% by weight nitrogen. Since each run consisted of four space velocities (10, 20, 40, 100), it was necessary to blend about 15 liters of feed per run. This quantity of feed was sufficient to run the unit until the nitrogen conversion reached a constant level and samples obtained.

**Catalyst and catalyst support:** Hydrodesulfurization work conducted previously at Montana State College in conjunction with the Esso Research and Engineering Company (9, 11) used a cobalt-molybdenum catalyst. From previous experience of hydrodenitrogenation and from the similar characteristics between desulfurization and denitrogenation, the Nalco-Esso cobalt-molybdenum 1/16-inch extruded catalyst was used. This catalyst is a mixture of cobalt and molybdenum oxides on an alumina support.

The catalyst bed was supported in the reactor on the top and bottom by 1/8-inch alundum pellets which were obtained from the Norton Company. The alundum pellets were also used to dilute the
catalyst and thereby produce a larger catalyst zone. The catalyst was diluted 9 parts pellets to 1 part catalyst by volume. The catalyst dilution made it possible to use a larger portion of the reactor which aided in the control of reactor conditions.

**Hydrogen Treat Gas:** The hydrogen treat gas was supplied in high pressure cylinders by HR Oxygen and Supply, Billings, Montana. The hydrogen was first passed through a "Deoxo" to remove trace quantities of oxygen. A palladium catalyst in the "Deoxo" unit catalytically combined the oxygen with hydrogen to form water. The water was then removed by passing the hydrogen through a drying unit which was packed with "Drierite".

**C. Equipment**

**Flow Diagram:** A schematic flow diagram of the catalytic hydrogenation unit is shown in Figure 1. The feed is pumped to the top of the reactor where it enters along with the purified hydrogen. Together the feed and hydrogen pass down through the preheater, catalyst, and after-heat zone. The vapors are condensed first in a counter current water condenser while still under reactor pressure. After passing through the reactor pressure regulator, the gas and liquid products are then passed through a cooling coil contained in an ice bath. The liquid product is collected in a flask while the gaseous product is vented to the atmosphere.
Equipment Specifications: The reactor was made from 1-inch OD, seamless, schedule 80, stainless steel pipe, and was 30 inches in length. The bottom of the reactor was silver welded to a flanged union to permit easy access to the inside of the reactor. The top of the reactor was permanently connected to a high pressure cross. A thermowell enters the reactor through the top of the cross. The feed and hydrogen enter the reactor through one side of the cross while the other is used as a safety device to vent the reactor to the atmosphere. A 1500 psi rupture disk was used for this purpose.

The reactor was wrapped with five ceramic-beaded nichrome heating coils. The heating coils were covered with approximately 1-1/2 inches of magnesia insulation.

A thermowell extended down through the center of the reactor to the flanged union at the bottom. A 3/16-inch OD stainless steel tube, sealed at the lower end, was used for the thermowell. Inside the thermowell were placed five iron-constantan thermocouples which measured the temperature at various levels through the reactor. A diagram of the location of heating coils, thermocouples, and catalyst zone are shown in Figure 2.

Accessory equipment was also utilized in the hydrogenation unit as follows: A Hills-McCanna high pressure proportioning pump with a 1/8-inch piston; a Brooks armored high pressure rotometer with 3/32-inch ball; a Grove back pressure regulator; five
110 volt Powerstats; a 1000 ml glass feed reservoir with a 50 ml graduated burette attached through a side arm, a Leeds and Northrup indicating potentiometer; four Marshalltown 2000 psi test gauges; a Dohor Deoxo Purifier; a Matheson hydrogen regulator.

The tubing used on the unit was type 304 stainless steel, 1/8-inch OD tubing.

Various types of valves used on the unit are as follows:
Hoke on-off valve; Hoke turn-to-open needle valve; Hoke micro-adjusting needle valve used for hydrogen metering.

D. Operating Procedures

Reactor Preparation: Once the reactor is dismantled from the system it is cleaned and dried before recharging. The reactor is inverted to expose the annular space between the reactor wall and the thermowell. The alumina pellets were first charged into the reactor to a selected depth. This forms the feed preheat section of the reactor. The catalyst that had been diluted with pellets was then charged into the reactor and packed by tapping. The length of the catalyst zone was kept as uniform as possible for each run. The reactor was then filled to about one inch below the flange with more catalyst support. A stainless steel coil was then secured on the bottom of the reactor to hold the catalyst and catalyst support in place when it was turned up into its normal position. The reactor was then coupled into its position in
the system.

The feed and gas line, the thermocouple leads, and the Powerstat cords were then connected to the reactor. Once the reactor was pressurized, the unit was checked for leaks.

After the reactor was brought to a temperature of 288° C, a gas mixture of 5% hydrogen sulfide and 95% hydrogen was passed over the catalyst for a period of 24 hours at a reactor pressure of 250 psig. This procedure was used for catalyst hydrogenation run starts.

**Reactor Operation:** Before the actual run was started, the reactor was changed from the break-in temperature to the desired temperature for that particular run. Once the pump was started it was necessary to adjust the pumping rate to the desired rate. This was done by a micro-adjustor on the pump that changed the stroke length of the piston. The space velocity was set to the desired value by measuring the volumetric oil feed rate. As the feed and hydrogen entered the reactor it was necessary to adjust the preheat Powerstat to heat the incoming feed to reactor temperature. The temperatures through the reactor were recorded, and the Powerstats were continually adjusted to maintain the desired constant temperature. The product passed out of the reactor and the liquid was collected in a flask until a product sample was taken.
Sampling: Before a product sample was taken, it was necessary to wait for the reactor to line out and thereby produce a reasonably constant conversion. Ryffel (13) found in his investigation of quinoline that from 6 to 8 hours of line-out time was sufficient to insure a constant conversion. After sufficient line-out time, a sample of about 50 cc was taken in a 500 ml flask. This sample was followed by another sample at approximately 1 hour later. In most cases both samples were analyzed and the average of the two conversions was used. Since the various amines are in vapor phase while in the reactor, it was necessary to be sure that all of the amines that had not been converted to ammonia were condensed and collected in the product sample. To insure this, the liquid product and the gas product were passed through an additional condenser after passing through the Grove regulator. This condenser was a stainless steel coil that was maintained in an ice bath.

At the beginning of the study, the additional condenser was not used. In Figure 3, two runs of identical conditions are plotted, except during one of the runs, the additional condenser was employed. It can be seen that the ice-bath had considerable effect on fully recovering the unreacted amines from the gas product stream. Additional procedures were employed in an effort to determine if there was an appreciable loss of amines from the product due to carry over but this could not be fully
E. Analytical Procedures

The nitrogen content of each product sample was determined by the standard Kjeldahl method (8). For each run it was necessary to determine the nitrogen content of the feed, as well as the nitrogen content of the various samples. Each determination was run in duplicate to insure accuracy, and the average of the two trials was used.

Samples from the runs which studied the effect of hydrogenation of the isomers of n-butyl amine were further analyzed with a vaporphase chromatography unit. The use of this unit made it possible to examine the various intermediates and products formed upon hydrogenation. This work was accomplished with an Aerograph Model A-110-C gas chromatograph in conjunction with a Brown-Honeywell Model 143 x 57 1 mv recorder.
III DISCUSSION OF METHODS OF DATA ANALYSIS

The rate of a chemical reaction is expressed quantitatively as the mass or moles of a product produced, or reactant consumed, per unit time \( (1^4) \). The rate of reaction can also be termed the velocity or speed of a specific reaction. Since the mass or moles of a product or reactant are usually expressed as a concentration, the rate of reaction is dependent upon the change of concentration with time.

If the rate is based on the change of concentration \( (C) \) of the reactant with time \( (t) \), the rate of reaction \( (r) \) can be expressed as:

\[
r = - \frac{dc}{dt}
\]

since the concentration of the reactant is decreasing.

The law of mass action states that the rate of a chemical reaction is proportional to the product of the 'active masses' of the reactants involved. Since the activity of a substance in a mixture is frequently difficult to obtain, concentrations are usually used to replace the active mass terms. For example, in the reaction

\[
A + B \rightarrow R + S
\]

we can express the rate as

\[
r = - \frac{dC_A}{dt} = kC_A^aC_B^b
\]

where \( r \) is the rate, \( C_A \) and \( C_B \) are the concentration of the respective reactants \( A \) and \( B \) and \( a \), \( b \), and \( k \) are constants. The constant \( k \) in the above equation is termed the 'specific reaction rate constant', or simply the 'rate constant'. In general, its units depend upon those employed for the con-
centration and upon the order of reaction. The order of reaction is defined as the sum of the exponents $a$ and $b$. Reactions orders may have values of 0, 1, 2, 3, or some fractional value. This derivation of the rate equation based upon the law of mass action is theoretically valid only for homogeneous systems. However, it has been found that data from heterogeneous systems can also be correlated quite well in many cases. This is particularly true when one of the reactants is present in large excess.

In a heterogeneous catalytic reaction, a factor must also be included in the rate equation to account for the preparation, composition, and physical properties of the catalyst. Thus for the overall reaction of

Quinoline + Hydrogen $\rightarrow$ Hydrocarbons + Ammonia

the rate could be expressed as:

$$ r = -\frac{\text{d}C_Q}{\text{d}t} = k \frac{C_Q C_H}{k_1} $$

where $k$ is the rate constant, $z$ is the catalyst factor, and $C_Q$ and $C_H$ are the concentrations of quinoline and hydrogen, respectively. This is, of course, assuming constant temperature and pressure."(13)

The above equation for this particular study would be replaced by the reaction:

Amines + Hydrogen $\rightarrow$ Hydrocarbons + Ammonia

If a large concentration of hydrogen is used, the change in concentration of hydrogen is negligible and therefore the concentration is assumed to be constant. For any one given catalyst, the factor $z$ is a constant and can be combined with the rate constant $R_1$ to form a new constant $R_2$. Since the product from the reaction is analyzed for nitrogen, and the nitrogen concentration of the feed is also known, it is advisable to base the change of concentration
in the reaction on the concentration of the nitrogen rather than the particular nitrogen compound. This changes the above rate equation to the new form:

\[ r = -\frac{dC_n}{dt} = k_e C^n_N \]  

(1)

Since the amount of nitrogen remaining in the sample is analyzed the difference between the initial concentration (A) and the amount converted (x), is determined. This quality (A-x) can then be substituted for \( C_N \) in equation (1). Also, the symbol \( \Theta \) is used to represent time by common convention. Equation (1) becomes:

\[ r = \frac{dx}{d\Theta} = k_e (A-x)^n \] 

(2)

Since the actual contact time is virtually impossible to determine, some proportional measure of contact time must be used. The term space velocity is used and it is based upon the volume or weight of reacting mass per unit volume or weight of catalyst per unit time. Since both the feed and catalyst are measured in the same units, space velocity has the unit of reciprocal time. By using the reciprocal of space velocity, this quantity can be substituted for the actual contact time in the above equation. For this study, the space velocity was determined by the weight of feed in grams to the weight of the catalyst in grams per hour.

If equation (2) is rearranged and integrated from \( x = 0 \) to \( x = x \) and \( \Theta = 0 \) to \( \Theta = \Theta \), the following is true:

\[ \int_0^x \frac{dx}{(A-x)^n} \equiv K_e \Theta = \frac{K_e}{S_V} \] 

(3)
where θ is also replaced by \( \frac{1}{S_Y} \).

The order of the reaction is then equal to the exponent (n) in equation (3). In arriving at this equation, it was assumed the hydrogen concentration was a constant; therefore, the order of the reaction is termed "pseudo order".

For experimental methods of determining order of reaction, the different orders are usually assumed until one is found which agrees with the experimental data. The agreement between the order of reaction tested and the data is usually tested visually until the data looks as though it fits quite well. If additional assurance is needed, statistical methods can be used to further verify the exactness of the results. Under any condition, however, the data points should not show a definite upward or downward trend.

In this study, the following orders were assumed and tested:

\( n = 1, \frac{3}{2}, 2 \). For the case of \( n = 1 \)

\[
\int_0^x \frac{dx}{A-x} = \frac{K_e}{S_Y}
\]

which integrates to give \( \ln(A/A-x) = K_e/S_Y \). A plot of \( \ln(A/A-x) \) vs \( 1/S_Y \) would then yield a straight line with a slope of \( K_e \) and an intercept of zero.

To study reaction orders of \( \frac{3}{2} \) and 2, the following should be plotted and the results examined to determine if the data yields a straight line:

\( n = \frac{3}{2} \) Plot \( 2/(A-x)^{1/2} \) vs \( 1/S_Y \) Intercept = \( 2/A^{1/2} \)
n = 2  Plot  \( \frac{1}{(\Lambda-x)} \) vs \( \frac{1}{S_Y} \)  Intercept - \( \frac{1}{\Lambda} \)

This discussion is based on the assumption that the reaction is
Amines + Hydrogen \( \rightarrow \) Hydrocarbons + Ammonia. From the analysis obtained from the chromatograph it was evident that no intermediates that contained nitrogen were formed. It is reasonable to assume that the nitrogen compounds were entirely converted to ammonia or else remained in the sample as the original nitrogen compound.
IV DISCUSSION OF RESULTS

The data from this study were first examined in the manner outlined previously. Two hydrogenation runs were selected for the study of possible reaction rates. The two runs chosen for this analysis were selected on the basis that they best represented the characteristics of all the data, and because these runs were conducted with some of the operating conditions similar to each of the other runs.

The operating conditions along with the initial feed concentration changed with each run. Since this information is only used in analyzing the data, it is not generally referred to in this report. These data are given in Table II. Also, the data contained in Tables III, IV, V, and VI, are the data used for constructing Figures 4 through 10.

Figure 4 is a plot of ln A/(A-x) vs reciprocal space velocity. Since the data do not even resemble a straight line through the origin for either run, it is assumed the reaction rate between n-butylamine and hydrogen under the given conditions is not first order. Similarly, Figures 5 and 6 are plots to determine if the reaction is second order or 3/2 order, respectively. In Figure 5, 1/(A-x) is plotted vs reciprocal space velocity with the intercept equal to 1/A. In this figure, the run conducted at 250 psig reactor pressure comes closer to fitting a straight line, but is
still not accurate enough to assume a second-order reaction. Figure 6 indicates clearly that the reaction rate is not of the order 3/2.

From the basis of this analysis, it is assumed that the reaction rate is not of common order. This does not eliminate the possibility of an empirical equation that could express the reaction rate for hydrogenation of n-butyl amine. It is possible that the reaction is controlled by some particular step which must first occur before the actual hydrogenation reaction is completed. For example, if it is first necessary to form a carbonium ion from the amine before the reaction can occur, then this rearrangement would conceivably be the controlling step in the reaction. The possibilities of actually forming carbonium ions in such a reaction are discussed later. Since more extensive studies were not conducted into possible reaction controlling steps, an overall reaction rate expression cannot be determined.

In an effort to compare the results of these runs, a common basis was chosen for the analysis of all the data. The method chosen was to handle the data in a manner similar to that for a first order reaction. This method was chosen for two reasons. Since this work was carried on in conjunction with the Esso Research and Engineering Company, the data were analyzed in the form of a first order reaction so that both groups used the same method of data analysis. Secondly, it has been shown that the rate of reaction for the
hydrogenation of quinoline under somewhat similar operating conditions was of first order (13).

A. **Effect of temperature**: The effect of temperature on hydrodenitrogenation between the temperatures of 625 to 725°F is shown in Figure 7. For a plot of ln \( A/(A-x) \) vs reciprocal space velocity, the curves should have an intercept of zero. This condition is true both from integrating the reaction rate equation and from the fact that at an infinite space velocity, the conversion would be zero.

At high space velocities, it became increasingly more difficult to maintain constant temperature through the catalyst zone. At a space velocity of 100, the upper part of the catalyst zone was not maintained at the desired temperature. This happened because it became impossible for the preheat zone to supply sufficient heat to bring such a large volume of feed up to reactor temperature. For this reason the data obtained at a space velocity of 100 were not included in this temperature study. The data for space velocities of 40 or less were obtained at constant temperature conditions.

From Figure 7, it is evident that an increase in temperature of 50°F through the reactor was sufficient to increase the conversion considerably. As an example, the data obtained at a space velocity of 20 can be used to compare the amount of nitrogen
removed for each temperature. At this space velocity the catalyst zone could be maintained at constant temperature, but yet the conversion was not high enough to create possible inaccuracies in the nitrogen content determination. At this space velocity the percent of nitrogen removed at the temperatures of 625, 675, and 725°F respectively were 66.8%, 73.2%, and 80.0%. This indicates that over this temperature range an increase of 50°F created a corresponding increase of approximately 6.6% in the total amount of nitrogen removed.

B. Effect of pressure: The effect of pressure on hydrode-nitrogenation for n-butyl amine between the pressures of 100 and 500 psig is shown in Figure 8. Figure 8 is a plot of ln A/(A-x) vs. reciprocal space velocity.

As the pressure increased, the conversion increased rapidly. For a pressure of 100 psig, a space velocity of 10 gave a conversion of approximately 65%. At a pressure of 500 psig, the space velocity was increased to 100 and still gave a conversion higher than at a space velocity of 10 for a reactor pressure of 100 psig. The conversion at a pressure of 500 psig and a space velocity of 100 was 65.8%, while a space velocity of 100 at 100 psig had a conversion of 35.8%.

Three runs were compared in Figure 8. All runs were made with a n-butyl amine feed. The pressures were 100, 250, and 500
psig. Again a space velocity of 20 was chosen for a comparison between conversions. The conversions for pressures of 100, 250, and 500 psig were 51.7%, 80.0%, and 95.2% respectively. At a space velocity of 10 and a pressure of 500 psig, there was essentially complete conversion.

C. Effect of molecular weight: As a comparison for molecular weight both n-butyl amine and n-octyl amine were studied. Normal octyl amine was hydrogenated at pressures of 100 and 500 psig and a temperature of 725°F. The results of these runs are plotted in Figure 9. Also, in Figure 9 similar runs with n-butyl amine are plotted for a comparison. At pressures of both 500 and 100 psig, the conversion is higher for n-butyl amine than for n-octyl amine. As the molecular weight increases, this trend toward more stable compounds would probably continue for other saturated aliphatic amines.

The product from the n-octyl amine study was examined for possible intermediate compounds. By use of the chromatograph it was possible to determine that the n-octyl amine was not cracked to form lower molecular weight hydrocarbons. Also, it was evident that the carrier, n-heptane, underwent very little cracking or change of composition.

D. Effect of structure on the hydrogenation of butyl amines: Figure 10 shows the effect of hydrogenation on the various isomers
of butyl amine. From the Figure it is evident that the ease of
denitrogenating the isomers decreases from tert-butyl amine, sec-
butyl amine, iso-butyl amine, to n-butyl amine in that order. As
a comparison between the conversions, a space velocity of 100 for
tert-butyl amine gave much higher conversions than did a space
velocity of 10 for n-butyl amine.

In an effort to justify this occurrence, various possible reac-
tion mechanisms were studied. The possible intermediates were
examined by use of a vapor-phase chromatograph. It was proposed
that the reaction occurred after the amine first went through a
rearrangement to form a carbonium ion. A carbonium ion is a group
of carbon atoms such that the carbonium ion carbon has only six
electrons in its valence shell (12). As an example of a carbonium
ion, iso-butyl amine can form the ion:

\[
\begin{align*}
\text{H}_3\text{C} & \\
\text{CH}_3 & \text{C}^+ \\
\text{H}_3\text{C} & 
\end{align*}
\]

This ion can then react with a hydrogen ion from the catalyst to
form the hydrocarbon isobutane.

The identification of the reaction products and intermediates
was accomplished by using the method of vapor-phase chromatography.
A vapor-phase chromatograph works essentially as a highly efficient
distillation column. However, it allows the analysis of very small
samples in a matter of minutes. The sample under investigation is
injected into the unit and is carried by a stream of helium into the packed column where it is selectively absorbed on the substrate. The absorption properties of each compound determine their respective retention times in the column. The stream of gas emerging from the column passes through a sensing element which measures its thermal conductivity and compares it to a standard (helium). This change in thermal conductivity is shown on a continuous chart recorder as a series of peaks, one for each compound as it emerges from the column. Thus, by identifying each peak by comparing it to peaks created from known compounds, it is possible to determine the various intermediates or products formed in a reaction (13).

Samples studied by this method were:

1. n-butyl amine under high conversion.
2. iso-butyl amine under high conversion.
3. sec-butyl amine under high conversion.
4. tert-butyl amine under high conversion.
5. n-butyl amine under low conversion.
6. iso-butyl amine under low conversion.
7. sec-butyl amine under low conversion.
8. tert-butyl amine under low conversion.
9. iso-butyl amine with acid wash.
10. tert-butyl amine with acid wash.

The chromatograms of the above studies are included in Figures 11 and 12. In these figures, the various products formed are also identified.

The proposed mechanism for hydrodenitrogenation of the isomers of butyl amine is essentially that of a carbonium ion rearrangement.
Both n-butyl amine and iso-butyl amine form the carbonium ion before reacting. The sec-butyl amine reacts directly without rearrangement while tert-butyl amine reacts as a carbonium ion since it is already in that form (12).

Samples from these runs, which had very high conversions, seemed to uphold this theory. This assumption is based on the fact that the carbonium ion must first be formed before the reaction can occur. Because of this, some of the hydrocarbons produced must appear in the product as isobutane. Figure 11 shows the results of this investigation.

The difference between the isobutane curve and the n-butane curve is labeled (A) on Figure 11. By comparing these curves to the curves produced from the product samples, it is possible to distinguish the various hydrocarbons which were formed. Part (B) of Figure 11 shows the effect of the n-butyl amine sample. By comparison, it is evident that some isobutane is formed from n-butyl amine. Also, Part (C) shows that iso-butyl amine produces essentially isobutane at high conversions. Part (D) indicates that sec-butyl amine does not produce any isobutane; therefore, the carbonium ion was probably not formed before denitrogenation occurred. Finally, Part (E) indicates that tert-butyl amine produced isobutane upon reaction. This analysis at high conversions tends to uphold the carbonium ion rearrangement as a possible intermediate step in the
reaction.

As a further check, samples from the same studies at low conversions were examined. Part (A) of Figure 12 indicates that at lower conversions, n-butyl amine still produces some isobutane and Part (B) indicates that sec-butyl amine still forms only n-butane. However, iso-butyl amine and tert-butyl amine indicate that there is some other intermediate formed in addition to the isobutane. This is shown as Part (C) and (D) in Figure 12. The possibility that these two compounds form an intermediate of n-butane is difficult to understand or explain. In an effort to determine the nature of this intermediate compound, the samples were acid-washed before being examined on the chromatograph. The samples after acid wash are Part (E) and (F) of Figure 12, iso-butyl amine and tert-butyl amine, respectively. However, from the figure it is evident that the acid wash did not remove the intermediates. If these intermediates had been unsaturated or perhaps some amine, the acid wash should have removed these compounds. Since the carrier has been shown to not be affected by the hydrogenation, it is difficult to determine fully the nature of these intermediates. The true mechanism for these reactions cannot be fully determined without further investigation.

The feed samples for each compound were also examined for impurities, but since no impurities were found, this analysis is
not reported in the appendix.

The possibility that these compounds must form various intermediates before reacting may be part of the reason that the reaction rate could not be expressed as some simple order.

By assuming such a mechanism for the hydrogenation, it would then be possible to explain the order in which these compounds denitrogenated. Using the carbonium ion mechanism as an example, the following may occur. If the tert-butyl amine did not rearrange and was already in a form which caused direct reaction, then it would yield the highest conversions. If the secondary compound also did not rearrange, but was not in the same active state as tert-butyl amine, then it would yield high conversions but not as high as tert-butyl amine.

The iso-butyl amine would undergo some rearrangement, but not as much as would n-butyl amine. This would cause the iso-butyl amine to react faster than the n-butyl amine. This, then, means that the amines reacted in the order with this rearrangement mechanism. From Figure 10, it can be seen that these compounds did denitrogenate in this particular order.
V CONCLUSIONS

The data from the hydrodenitrogenation study were first examined for possible pseudo reaction rate order. It was determined that the reaction rate was not of common order. From the chromatograph analysis, it was evident that n-butyl amine formed intermediate compounds upon hydrogenation. The formation of intermediates could be rate controlling, causing the order of reaction rate to be of uncommon order.

The effect of temperature was studied on n-butyl amine. It was shown that an increase in temperature increased the total nitrogen conversion. At a space velocity of 20, an increase in temperature of 50°F increased the total conversion by 64%.

An increase in pressure increased the total nitrogen conversion considerably. At a space velocity of 100, the conversion was 65.8% at 500 psig as compared to a conversion of 35.8% at 100 psig.

By comparing n-butyl amine to n-octyl amine, it was evident that the lower molecular weight compound reacted to give higher conversions. This condition held for pressures of 100 and 500 psig.

The conversions for the isomers of butyl amine decreased in the order of tertiary, secondary, iso, and normal butyl amine. This order may be accounted for by the various mechanisms needed for each compound to denitrogenate.
The author would like to take this opportunity to acknowledge and thank the Esso Research and Engineering Company that sponsored this research project and supplied many materials used throughout the investigation. He also wishes to thank the staff of the Chemical Engineering Department for their helpful suggestions and criticisms; and in particular, Doctor Lloyd Berg who directed this research. He would also like to thank Mr. G. P. Schreiber, fellow research worker, for his assistance on this project.
VII. LITERATURE CITED


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TABLE I
EFFECT OF ICE, BATH ON SAMPLING

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conversion</th>
<th>Space Velocity</th>
<th>Ice Bath</th>
<th>Sample No.</th>
<th>Conversion</th>
<th>Space Velocity</th>
<th>Ice Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-12</td>
<td>0.060</td>
<td>0.10</td>
<td>No</td>
<td>N-24-2</td>
<td>0.108</td>
<td>1.0</td>
<td>Yes</td>
</tr>
<tr>
<td>N-2-6</td>
<td>1.262</td>
<td>0.20</td>
<td>No</td>
<td>N-24-4</td>
<td>0.202</td>
<td>2.0</td>
<td>Yes</td>
</tr>
<tr>
<td>N-10</td>
<td>3.576</td>
<td>4.00</td>
<td>No</td>
<td>N-24-6</td>
<td>3.87</td>
<td>4.0</td>
<td>Yes</td>
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</table>

Uniform Operating Conditions:

Feed: 1% n-butyl amine
Temperature: 725°F
Pressure: 250 psig
Weight of Catalyst: 10 g.
**Table II**

**Operating Conditions and Initial Feed Concentrations**

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed</th>
<th>Feed Conc. Wt. % N</th>
<th>Temp. °F</th>
<th>Press. Psig</th>
<th>Space Velocities</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-14</td>
<td>n-butyl amine</td>
<td>0.984</td>
<td>675</td>
<td>250</td>
<td>10, 20</td>
</tr>
<tr>
<td>N-16</td>
<td>n-butyl amine</td>
<td>0.978</td>
<td>625</td>
<td>250</td>
<td>10, 20</td>
</tr>
<tr>
<td>N-17</td>
<td>octyl amine</td>
<td>1.050</td>
<td>725</td>
<td>500</td>
<td>10, 20, 40, 100</td>
</tr>
<tr>
<td>N-18</td>
<td>n-butyl amine</td>
<td>1.014</td>
<td>725</td>
<td>500</td>
<td>10, 20, 40, 100</td>
</tr>
<tr>
<td>N-19</td>
<td>sec-butyl amine</td>
<td>1.027</td>
<td>725</td>
<td>250</td>
<td>10, 20, 40, 100</td>
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<tr>
<td>N-20</td>
<td>iso-butyl amine</td>
<td>1.022</td>
<td>725</td>
<td>250</td>
<td>10, 20, 40, 100</td>
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<tr>
<td>N-21</td>
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<td>725</td>
<td>250</td>
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<td>100</td>
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<td>n-butyl amine</td>
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<td>725</td>
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<td>10, 20, 40, 100</td>
</tr>
<tr>
<td>N-24</td>
<td>n-butyl amine</td>
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<td>725</td>
<td>250</td>
<td>10, 20, 40</td>
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<tr>
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<td>n-butyl amine</td>
<td>1.008</td>
<td>625</td>
<td>250</td>
<td>40</td>
</tr>
</tbody>
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Uniform Operating Conditions:

- Pressure: 250 psig
- Weight of Catalyst: 10 g
- Hydrogen Rate: 500 SCF of H₂/bbl of Feed
### Table III

#### Data for Test of Reaction Order

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space Velocity $S_v$</th>
<th>Pressure Psig</th>
<th>$1/S_v$</th>
<th>A-x</th>
<th>A</th>
<th>$\ln A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-23-2</td>
<td>20</td>
<td>100</td>
<td>.05</td>
<td>.505</td>
<td>2.07</td>
<td>.728</td>
</tr>
<tr>
<td>N-23-4</td>
<td>10</td>
<td>100</td>
<td>.10</td>
<td>.365</td>
<td>2.87</td>
<td>1.054</td>
</tr>
<tr>
<td>N-23-6</td>
<td>40</td>
<td>100</td>
<td>.025</td>
<td>.605</td>
<td>1.73</td>
<td>.548</td>
</tr>
<tr>
<td>N-23-8</td>
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<td>100</td>
<td>.01</td>
<td>.671</td>
<td>1.56</td>
<td>.443</td>
</tr>
<tr>
<td>N-24-2</td>
<td>10</td>
<td>250</td>
<td>.10</td>
<td>.108</td>
<td>9.38</td>
<td>2.23</td>
</tr>
<tr>
<td>N-24-4</td>
<td>20</td>
<td>250</td>
<td>.05</td>
<td>.202</td>
<td>4.99</td>
<td>1.61</td>
</tr>
<tr>
<td>N-24-6</td>
<td>40</td>
<td>250</td>
<td>.025</td>
<td>.387</td>
<td>2.61</td>
<td>.96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{1}{A-x}$</th>
<th>$\frac{2}{A-x}$</th>
<th>$\frac{1}{A}$</th>
<th>$\frac{2}{A}$</th>
<th>$A$</th>
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</thead>
<tbody>
<tr>
<td>N-23-2</td>
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<td>2.814</td>
<td>.957</td>
<td>1.955</td>
<td>1.045</td>
</tr>
<tr>
<td>N-23-4</td>
<td>2.74</td>
<td>3.31</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>N-23-6</td>
<td>1.65</td>
<td>2.57</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>N-23-8</td>
<td>1.49</td>
<td>2.44</td>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
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<td>.996</td>
<td>1.99</td>
<td>1.008</td>
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<tr>
<td>N-24-4</td>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
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<td>N-24-6</td>
<td>2.59</td>
<td>3.22</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

#### Uniform Operating Conditions

- **Feed:** 1% n-butyl amine
- **Temperature:** 725°F
- **Weight of Catalyst:** 10 g
- **Hydrogen Rate:** 500 SCF of H₂/bbl of Feed
### TABLE IV

**DATA FOR EFFECT OF TEMPERATURE ON HYDROGENATION**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space Velocity v/v</th>
<th>Temp. °F</th>
<th>A-x</th>
<th>A/A-x</th>
<th>ln (A/A-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-24-2</td>
<td>10</td>
<td>725</td>
<td>.108</td>
<td>9.24</td>
<td>2.23</td>
</tr>
<tr>
<td>N-24-4</td>
<td>20</td>
<td>725</td>
<td>.202</td>
<td>4.99</td>
<td>1.61</td>
</tr>
<tr>
<td>N-24-6</td>
<td>40</td>
<td>725</td>
<td>.387</td>
<td>2.61</td>
<td>.96</td>
</tr>
<tr>
<td>N-14-4</td>
<td>20</td>
<td>675</td>
<td>.265</td>
<td>3.71</td>
<td>1.31</td>
</tr>
<tr>
<td>N-14-6</td>
<td>10</td>
<td>675</td>
<td>.142</td>
<td>6.93</td>
<td>1.93</td>
</tr>
<tr>
<td>N-16-2</td>
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<td>625</td>
<td>.325</td>
<td>3.01</td>
<td>1.10</td>
</tr>
<tr>
<td>N-16-4</td>
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<td>625</td>
<td>.222</td>
<td>4.4</td>
<td>1.48</td>
</tr>
<tr>
<td>N-24-8</td>
<td>40</td>
<td>625</td>
<td>.526</td>
<td>1.92</td>
<td>.652</td>
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</tbody>
</table>

**Uniform Operating Conditions:**

- **Feed:** 1% n-butyl amine
- **Pressure:** 250 psig
- **Weight of Catalyst:** 10 g
- **Hydrogen Rate:** 500 SCF of H₂/bbl
### TABLE V

**DATA FOR EFFECT OF PRESSURE ON HYDROGENATION**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space Velocity v/v</th>
<th>Press. Psig</th>
<th>A-x</th>
<th>( \frac{A}{A-x} )</th>
<th>ln ( \frac{A}{A-x} )</th>
<th>Feed</th>
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</thead>
<tbody>
<tr>
<td>N-23-2</td>
<td>.20</td>
<td>.100</td>
<td>.505</td>
<td>22.007</td>
<td>.728</td>
<td>n-butyl amine</td>
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<tr>
<td>N-23-4</td>
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<td>.365</td>
<td>2.87</td>
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</tr>
<tr>
<td>N-23-6</td>
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<td>.100</td>
<td>.605</td>
<td>1.73</td>
<td>.548</td>
<td></td>
</tr>
<tr>
<td>N-23-8</td>
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<td>.100</td>
<td>.671</td>
<td>1.56</td>
<td>.443</td>
<td></td>
</tr>
<tr>
<td>N-24-2</td>
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<td>250</td>
<td>.108</td>
<td>9.34</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>N-24-4</td>
<td>20</td>
<td>250</td>
<td>.202</td>
<td>4.99</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>N-24-6</td>
<td>40</td>
<td>250</td>
<td>.387</td>
<td>2.61</td>
<td>.96</td>
<td></td>
</tr>
<tr>
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<td>500</td>
<td></td>
<td>complete conversion</td>
<td>--</td>
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<tr>
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<td>.169</td>
<td>6.00</td>
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<td>1.643</td>
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<td>100</td>
<td>.520</td>
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<td>N-22-6</td>
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<td>100</td>
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<td>1.396</td>
<td>.259</td>
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<td>11.0</td>
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</tr>
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<td>N-17-4</td>
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<td>500</td>
<td></td>
<td>conversion too high</td>
<td>--</td>
<td></td>
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**Uniform Operating Conditions:**

- **Feed:** 1% n-butyl amine, 1% n-octyl amine
- **Temperature:** 725°F
- **Weight of Catalyst:** 10 g.
- **Hydrogen Rate:** 500 SCF of H₂/bbl of Feed
### TABLE VI

**EFFECT OF STRUCTURE ON HYDROGENATION OF BUTYL AMINE**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed</th>
<th>Space Velocity</th>
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<th>A/A-x</th>
<th>ln A/A-x</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-24-2</td>
<td>n-butyl amine</td>
<td>10</td>
<td>.108</td>
<td>9.34</td>
<td>2.23</td>
</tr>
<tr>
<td>N-24-4</td>
<td>&quot;</td>
<td>20</td>
<td>.202</td>
<td>4.99</td>
<td>1.61</td>
</tr>
<tr>
<td>N-24-6</td>
<td>&quot;</td>
<td>40</td>
<td>.387</td>
<td>2.61</td>
<td>.96</td>
</tr>
<tr>
<td>N-21-8</td>
<td>tert-butyl amine</td>
<td>100</td>
<td>.0388</td>
<td>25.5</td>
<td>3.24</td>
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<td>N-20-2</td>
<td>iso-butyl amine</td>
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<td>.0739</td>
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<td>40</td>
<td>.319</td>
<td>3.21</td>
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<td>.531</td>
<td>1.927</td>
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<td>N-19-8</td>
<td>sec-butyl amine</td>
<td>.100</td>
<td>.1480</td>
<td>6.94</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Uniform Operating Conditions:

- Temperature: 725°F
- Pressure: 250 psig
- Weight of Catalyst: 10 g
- Hydrogen Rate: 500 SCF of H₂/bbl
Figure 1. Schematic Flow Diagram of Hydrogenation Unit
Figure 2. Detailed Diagram of Reactor
Figure 3. Effect of Ice Bath on Sampling
Temp. 725°F
Feed 1% n-butyl amine
○ - 250 psig
△ - 100 psig

Figure 4. Test for Pseudo First Order Reaction
Figure 5. Test for Pseudo Second Order Reaction
Figure 6. Test for Pseudo Reaction Order of 3/2
Figure 7. Effect of Temperature on Hydrogenation
Figure 8. Effect of Pressure on Hydrogenation
Figure 9. Effect of Pressure on Hydrogenation of n-octyl Amine, and Effect of Molecular Weight on Hydrogenation
Figure 10. Effect of Structure on Hydrogenation of Butyl Amine
Figure II. Chromatogram for High Conversion Samples

1. Air and Ammonia
2. Isobutane
3. n-Butane
4. 1-Butene
5. Isobutane + n-Butane feed
6. n-Butyl amine sample
7. Isobutyl amine sample
8. sec-Butyl amine sample
9. Tertiary Butyl amine sample
Figure 12. Chromatogram for Low Conversion Samples and Acid Washed Samples.

1. Air + Ammonia
2. Iso butane
3. n-butane
4. ... butyl amine sample
5. Iso-butyl amine sample
6. tert-butyl amine sample (acid washed)
7. tert-butyl amine sample (acid washed)
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