



The destructive catalytic hydrogenation of certain heterocyclic nitrogen compounds
by Kenneth Edward Cox

A Thesis Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Chemical Engineering
Montana State University
© Copyright by Kenneth Edward Cox (1961)

Abstract:

The destructive catalytic hydrogenation of some twenty-nine heterocyclic nitrogen compounds has been studied. The main aim of this study was to gather and evaluate kinetic data on the destructive catalytic hydrogenation of these compounds and to reach any conclusions governing their rates of hydrogenation.

The study was carried out on a bench scale, continuous, tubular flow reactor that was capable of handling feeds up to 500 ml/hour. The operating conditions chosen for this comparison study were: temperature 700°F, pressure 250 psig, hydrogen flow rate 7500 and 1000 SCF/bbl, space velocity 0.50 to 20.0 ml/ml/hour, and initial nitrogen concentration 0.3 Wt.% N. For the later study of the effect of initial concentration on the conversion for four of the above compounds, initial concentrations of 1.0 and 2.5 Wt.% N were chosen.

All calculations were based on the overall nitrogen concentration.

The destructive catalytic hydrogenation of most of the five member ring compounds investigated proved to be of second order, while that of most of the twenty-two six member ring compounds proved to be of first order under the above operating conditions.

It was noted that unsaturated nitrogen heterocyclics had higher reaction rate constants than did saturated nitrogen heterocyclics. This implies that the saturated compounds are easier to destructively hydrogenate than unsaturated ones. The reaction rate constants for groups of pyridine isomers were found to correlate linearly with their normal boiling points. No generalizations concerning the reaction rates of the other compounds studied could be found.

Linear and quadratic models were postulated for the regression of the percentage conversion on the process variables, initial nitrogen concentration and space velocity for the four compounds; pyrrole, pyrrolidine, pyridine and 2,6-lutidine. The linear model was found to be a fair estimate in all four cases, the average multiple correlation coefficient being 0.85. The quadratic model was found to be a better estimate than the linear model in all cases, multiple correlation coefficients for this model being in the neighborhood of 0.97.

THE DESTRUCTIVE CATALYTIC HYDROGENATION
OF CERTAIN HETEROCYCLIC NITROGEN COMPOUNDS

by

KENNETH E. COX

A Thesis

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of

Doctor of Philosophy in Chemical Engineering

at

Montana State College

Approved:

Head, Major Department

Chairman, Examining Committee

Dean, Graduate Division

Bozeman, Montana
December, 1961

D378

C838

cop.3

-2-

TABLE OF CONTENTS

	Page
Abstract -----	3
I Introduction -----	4
II Research Objectives -----	7
III Experimental Considerations -----	8
A. Introduction -----	8
B. Materials -----	10
C. Equipment -----	12
D. Operating Procedures -----	14
E. Analytical Procedures -----	16
IV Methods of Data Analysis -----	17
A. Empirical Rate Equation -----	17
B. Regression Analysis to Determine Fit of Proposed Reaction Order -----	20
C. Multiple Regression -----	23
V Discussion of Results -----	26
A. Introduction -----	26
B. Rate Equation - Five Member Ring Compounds -----	26
C. Rate Equation - Six Member Ring Compounds -----	28
D. Comparison of Reaction Rates, Saturated and Unsaturated Compounds -----	31
E. Multiple Regression of Percentage Conversion on Initial Concentration and Space Velocity -----	32
VI Conclusions -----	37
VII Acknowledgement -----	40
VIII Literature Cited -----	41
IX Appendix -----	43

ABSTRACT

The destructive catalytic hydrogenation of some twenty-nine heterocyclic nitrogen compounds has been studied. The main aim of this study was to gather and evaluate kinetic data on the destructive catalytic hydrogenation of these compounds and to reach any conclusions governing their rates of hydrogenation.

The study was carried out on a bench scale, continuous, tubular flow reactor that was capable of handling feeds up to 500 ml/hour. The operating conditions chosen for this comparison study were: temperature 700°F, pressure 250 psig, hydrogen flow rate 7500 and 1000 SCF/bbl, space velocity 0.50 to 20.0 ml/ml/hour, and initial nitrogen concentration 0.3 Wt.% N. For the later study of the effect of initial concentration on the conversion for four of the above compounds, initial concentrations of 1.0 and 2.5 Wt.% N were chosen.

All calculations were based on the overall nitrogen concentration. The destructive catalytic hydrogenation of most of the five member ring compounds investigated proved to be of second order, while that of most of the twenty-two six member ring compounds proved to be of first order under the above operating conditions.

It was noted that unsaturated nitrogen heterocyclics had higher reaction rate constants than did saturated nitrogen heterocyclics. This implies that the saturated compounds are easier to destructively hydrogenate than unsaturated ones. The reaction rate constants for groups of pyridine isomers were found to correlate linearly with their normal boiling points. No generalizations concerning the reaction rates of the other compounds studied could be found.

Linear and quadratic models were postulated for the regression of the percentage conversion on the process variables, initial nitrogen concentration and space velocity for the four compounds; pyrrole, pyrrolidine, pyridine and 2,6-lutidine. The linear model was found to be a fair estimate in all four cases, the average multiple correlation coefficient being 0.85. The quadratic model was found to be a better estimate than the linear model in all cases, multiple correlation coefficients for this model being in the neighborhood of 0.97.

I INTRODUCTION

At this time, the oil reserves of the United States and the world in general, are increasing with the increasing demand for oil. In fact, at present the supply of oil available in the United States exceeds the demand for it. However, with increasing demands from the petrochemical industry and other users of oil, a time may arrive in the foreseeable future when the demand for oil may exceed its supply. For this eventuality, petroleum refiners are seeking alternative sources of oil.

In 1944, the United States Congress passed the Synthetic Fuels Act which authorized research and development of new sources of oil. The main sources of petroleum substitutes in the United States are the vast beds of oil shale in Wyoming and Colorado, and liquid and gaseous products from coal hydrogenation (7). There are also large deposits of tar sands in Alberta, Canada which are also being developed in a move to solve the problem of insufficient oil in the future.

These sources, however, have the disadvantage of containing substantial quantities of nitrogen, oxygen and sulfur compounds in addition to the hydrocarbon compounds. Nitrogen, oxygen and sulfur compounds are undesirable in petroleum stocks as they cause catalyst deactivation, gum formation and color instability. (14) They are also noted for their unpleasant odor.

Thus, it appears that methods must be found to rid the stocks of these 'undesirable' compounds. Among the better methods available to

refiners is destructive catalytic hydrogenation. This involves passing the oil stock together with hydrogen over a suitable catalyst at high temperatures and pressures. The hydrogen reacts with the nitrogen compound, say, to give a hydrocarbon and ammonia.

It must be noted here that not all nitrogen compounds are undesirable. Some of them are used in the plastics and resins industries. These compounds are usually obtained from coal tar distillates. If a selective hydrogenation process were developed, a new route to these compounds may be opened.

The reactions involved in hydrogenating a complex mixture of nitrogen compounds that are contained in an oil stock are numerous and complex and thus extensive research must be undertaken in order to gain information on them.

Research involving shale oil fractions has been carried out at Montana State College since 1954 (13, 16). The literature (9) states that the majority of the nitrogen compounds found in shale oil and coal hydrogenate are homologs and derivatives of the following heterocyclic nitrogen compounds: quinoline, pyridine, and pyrrole. The destructive catalytic hydrogenation of quinoline has been studied extensively by Ryffel (16), and that of pyridine and pyrrole more recently by Schreiber (17). To add to this previous work, it was proposed to study the destructive catalytic hydrogenation of some of the derivatives of these compounds and to determine whether conclusions could be drawn regarding the ease or difficulty

of denitrogenation of these derivatives.

The information in this thesis is obtained from a study as outlined above. Due to the pure compounds and artificial feed stocks that were employed, the information in this thesis is of a fundamental rather than of a practical nature. It is felt, however, that some light has been shed on the hydrogenation of feeds containing heterocyclic compounds and it is hoped that some of the data obtained will be utilized in the further investigation of the destructive catalytic hydrogenation of naturally occurring feed stocks.

II RESEARCH OBJECTIVES

The aim of this research was to gather and evaluate data on the destructive catalytic hydrogenation of different types of heterocyclic nitrogen compounds.

The main purpose of this study was to obtain kinetic data so as to compare the rates of denitrogenation of these compounds, and to determine the order of reaction for reactions of different classes of these compounds.

We were also interested in obtaining empirical equations relating the percentage conversion to the variables, initial nitrogen feed concentration and space velocity, for four compounds that were representative of four different classes of the compounds.

The above objectives of this study were met insofar as time and equipment allowed. It is hoped that the results obtained in this fundamental study will be of use in the general problem of removing undesirable nitrogen compounds from feed stocks containing them.

III EXPERIMENTAL CONSIDERATIONS

A. Introduction

Selection of Feedstock: The literature has reported that nitrogen in naturally occurring stocks is present primarily as homologs and derivatives of quinoline, pyridine, and pyrrole (1, 2, 9, 19).

Extensive studies on quinoline have already been carried out at Montana State College by Ryffel (16), and on pyridine and pyrrole by Schreiber (17).

It was therefore decided to obtain as many as possible of the available derivatives of the above compounds for this study. In all, 29 such compounds were obtained. They are listed in Table I.

In order to prepare a feedstock that contained the desired amount of nitrogen as heterocyclics, it was necessary to choose a carrier that in barrel lots was reasonably priced and of sufficient purity. The carrier would also have to blend readily with the heterocyclic nitrogen compounds chosen for the study, and not affect the hydrogenation reaction in any way.

Some of the carriers used in the studies mentioned above included: Penetec (a mineral oil), toluene, methycyclohexane, normal heptane and cumene. Due to the excellent results obtained by Schreiber (17) with toluene as a carrier, and its excellent solubility properties with the heterocyclic compounds under study, toluene was selected as the carrier

liquid for this work.

Toluene is an aromatic liquid with a molecular weight of 92.13 and a boiling point at 760mm of 110.63°C (8). It proved to be miscible with all the liquid heterocyclic nitrogen compounds and it dissolved all the solid heterocyclics with the one exception of carbazole.

Process Conditions: The process conditions for this study were chosen from the previous knowledge gained at Montana State College of hydrogenation processes.

The initial nitrogen concentration in the feedstocks was chosen at 0.3 weight percent nitrogen for two main reasons. First, the nitrogen concentration in naturally occurring feedstocks to refining units is in the neighborhood of 0.3 weight percent nitrogen (2). Second, higher initial nitrogen concentrations would have necessitated an excessive amount of the pure nitrogen compound that made up the feed. In some cases this amount was limited due to the high purchase price of the nitrogen heterocyclic compound.

Space velocities were selected principally on the basis of percentage conversion, desirable conversions being in the 10-90 percent range.

The following process conditions were chosen at first:

Pressure:	Constant at 250 psig.
Temperature:	Constant at 700°F (371°C)
Hydrogen Flow Rate:	7500 SCF/bbl feed.
Initial Nitrogen	
Concentration:	0.3 Wt. percent.
Space Velocities:	0.5 to 20ml/ml/hour.
Catalyst:	Peter Spence Cobalt Molybdate 1/8" x 1/8", 6 to 120 ml.

At a later stage in the project, the hydrogen flow rate was adjusted from 7500 SCF/bbl feed to 1000 SCF/bbl feed in order to conserve hydrogen for economic reasons. The rate of 7500 SCF/bbl had previously been used to ensure excess hydrogen so that the hydrogenation reaction would be essentially independent of hydrogen concentration. An experimental run done on the same feedstock at these two rates, holding all other conditions constant, showed no significant difference in nitrogen conversion. It was therefore decided to carry out the remainder of the study under the same conditions but with the reduced hydrogen rate of 1000 SCF/bbl. Note that even at this relatively low hydrogen rate, the amount of hydrogen is still stoichiometrically adequate by several hundred percent.

B. Materials

Feedstock: The carrier liquid used was Phillips Petroleum Company technical grade toluene. The toluene came in 5-gallon drums and was labeled as 99 mol percent purity.

The feedstocks were prepared by mixing the correct amount of the pure nitrogen compound with the toluene to obtain the desired concentra-

tion of nitrogen. Approximately two liters of feedstock were prepared in this manner for each run.

The heterocyclic nitrogen compounds used in this study came from various sources. They are listed together with their main properties in Table I. Briefly, the following main classes of heterocyclics were obtained:

- Class 1: Five Member Ring - Unsaturated
- Class 2: Five Member Ring - Saturated
- Class 3: Six Member Ring - Unsaturated
- Class 4: Six Member Ring - Saturated
- Class 5: Compounds with more than a single ring.

Examples of the classes are as follows:

- Class 1: Pyrrole
- Class 2: Pyrrolidine
- Class 3: Pyridine
- Class 4: Piperidine
- Class 5: Indole

Twenty-nine compounds in all were obtained; the majority of the compounds are in Class 3, being derivatives of pyridine.

Catalyst and Catalyst Supports: Previous hydrodesulfurization and hydrodenitrogenation work conducted at Montana State College (5, 12), the Engineering Experiment Station (13), and reported in the literature (3) have shown that a cobalt-molybdenum oxide catalyst is effective in hydrogenation processes.

The catalyst used in this study was Peter Spence extruded catalyst, Type RD 3718, 1/8-inch by 1/8-inch, and consisted of 2.5% cobalt oxide

and 14% molybdenum oxide on an alumina carrier.

The catalyst bed was supported in the reactor, both on top and below by 1/8-in. and 1/4-in. alundum pellets that were obtained from the Norton Company. The catalyst and 1/8-in. pellets of alundum were diluted to occupy a volume of about 100 ml in the center of the reactor. This constituted the 'catalyst zone' of the reactor.

Hydrogen Treat Gas: The hydrogen treat gas was supplied in high pressure cylinders by HR Oxygen and Supply, Billings, Montana. The hydrogen gas was used as supplied in order to more closely simulate industrial conditions.

C. Equipment

Flow Diagram: A schematic flow diagram of the catalytic hydrogenation unit is shown in Figure 1. The reactor is operated as a fixed bed, continuous, tubular reactor. The feedstock is pumped to the top of the reactor where it enters with the hydrogen. The feed and hydrogen then pass down through the pre-heat, catalyst, and after-heat zones of the reactor. The reaction mixture is in the gas phase as it passes through the catalyst zone of the reactor. The vapors after reaction are condensed first in a counter-current water condenser under pressure. After passing through the reactor back-pressure regulator, the gaseous and liquid products are passed through another water condenser and finally through a cooling coil immersed in an ice bath to ensure complete liquid product recovery. The liquid product is collected in a flask while the gases are water-scrubbed before being vented to the atmosphere.

Equipment Specifications: The reactor was made from 1-in. OD seamless, schedule 80 stainless steel pipe 30 inches long. The bottom of the reactor was welded to a flanged union to permit easy access to the inside of the reactor. The top of the reactor was also welded to a flanged union. This was, in turn, permanently joined to a high pressure cross containing a 1500 psig rupture disc in one of its side arms. This rupture disc was inserted as a safety device. A thermowell entered the reactor through the top of the cross, and the feed and hydrogen mixture through the other side arm of the cross.

The reactor was wrapped with five ceramic-beaded nichrome heating coils. The heating coils were covered with approximately one inch of magnesia insulation. The heating coils were connected to a 110-volt constant voltage supply, and individual Variacs were used to regulate the current supply to the coils.

A thermowell extended down through the center of the reactor to within one inch of the bottom flange. A 3/16-in. OD stainless steel tube, sealed at the bottom end, was used for the thermowell. Four iron-constantan thermocouples were inserted at regularly spaced positions inside the thermowell for measuring the temperature at various locations through the reactor. The thermocouples were connected to a Leeds and Northrup indicating potentiometer which read directly in degrees. The diagram giving the cut-away view of the reactor and showing the locations of the thermocouples, heating coils, and catalyst zone is Figure 2.

Accessory equipment was used as follows: A Hills-McCanna high pressure proportioning pump with a 1/4-in. piston; a Brooks armored high pressure rotameter with a 3/32-in. stainless steel ball; a Grove (Mity-Mite) back pressure regulator; a 1000 ml glass feed reservoir attached to a 50 ml burette side arm; three Marshalltown pressure gages; and a Matheson hydrogen gas regulator. The tubing used on the unit was type 304 stainless steel, 1/8-in. OD tubing. Various Hoke valves were used where required on the unit.

D. Operating Procedures

Feed Stock Preparation: The feedstock was usually prepared the night before the run was to be made, the amount prepared being approximately two liters. The method of preparation was simply to add the required amount of the heterocyclic nitrogen compound to a given weight of toluene to produce the desired concentration.

Reactor Preparation: Before each run, the reactor, condenser, and back pressure regulator were washed with a suitable solvent. The main solvent being used for this purpose was acetone. After the reactor was dried of acetone, it was inverted on a special stand and filled with 1/4-in. alundum pellets to a desired level. This constituted the pre-heat section. The diluted new catalyst (diluted to a volume of 100 ml when necessary) was then added. The reactor was then filled to just below the flange with more 1/4-in. catalyst support. After tapping the reactor lightly to ensure proper settling of the catalyst and supports, a stainless steel screen followed by a stainless steel ring were

inserted in the bottom of the reactor, to keep the charge in place. The reactor was then coupled into its position in the system. The feed lines, thermocouple leads and Variac cords were then hooked onto the unit. It was then pressurized and tested for leaks. If no leaks were found, the unit was ready for a run.

Operation: The reactor was pressurized and left to heat overnight in a hydrogen atmosphere in preparation for a run. To start the run, the feed pump was started and set at the desired pumping flow rate. The hydrogen flow rate was metered on the rotameter and adjusted by means of a needle valve. The heater Variacs were then set at readings that gave the desired temperature through the reactor. Temperature control was manual. Temperatures were checked and logged every half hour and adjustments made to the corresponding Variacs when necessary. The reacted liquid product was collected after being cooled in an ice bath. The purpose of this ice bath was to condense completely all liquid product.

Sampling: Samples were taken three to six hours after constant process conditions, especially operating temperature, had been reached. This time period was to allow the unit to 'line out' in order to ensure constant conversion. A sample of about 60 ml was taken in a clean 500 ml flask. This sample was repeated by another sample at approximately one hour later. Both samples were analyzed and the conversions compared to see whether 'line out' conditions were met.

E. Analytical Procedure:

The total nitrogen content in the feed stock and in the samples was determined as weight percent nitrogen by the standard Kjeldahl method (11). Each determination was run in duplicate and the results were averaged. The percentage conversion was then calculated using these results and the feed stock concentration.

IV METHODS OF DATA ANALYSIS

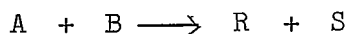
A. Empirical Rate Equation:

The rate of a chemical reaction may be expressed quantitatively as the mass or moles of a product produced, or a reactant consumed, per unit time (6, 18). The rate of reaction can also be termed the velocity or speed of a specific reaction. Since the mass or moles of product or reactant are usually expressed as a concentration, the rate of reaction is dependent on 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 written as:

$$r = \frac{-dC}{dt} \quad \text{-----}(1)$$

The law of mass action states that the reaction rate of a chemical reaction r is proportional to the products 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:



the rate may be expressed as:

$$r = \frac{-dC_A}{dt} = k C_A^a C_B^b \quad \text{-----}(2)$$

where r is the rate, C_A and C_B are the concentrations of the reactants A and B respectively, and a , b , k are constants.

The constant k in the above equation is termed the 'specific reaction rate constant' or more simply, the 'rate constant'. In general, the rate constant is constant only for a fixed set of operating conditions. The units of the rate constant depend upon the concentration units involved and the order of the reaction. The order of the reaction is defined as the sum of the exponents a and b . The order of a reaction may commonly have values from 0 to 3 including fractional values.

The rate equation derived above is strictly true only for homogenous systems. However, it has been found that data for heterogenous systems can also be correlated quite well in many cases. This is particularly true especially if one of the reactants is present in a large excess.

For a heterogenous catalytic reaction, the rate equation may be expressed as:

$$r = \frac{-dC_A}{dt} = k_1 Z C_A^a C_B^b \quad \text{-----}(3)$$

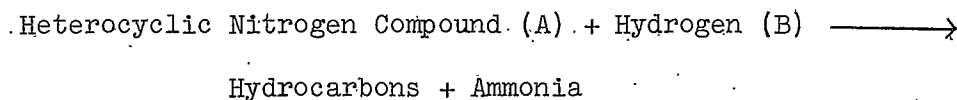
assuming constant temperature and pressure, where:

k_1 is the rate constant

C_A and C_B are the concentrations of A and B

Z is the 'catalyst factor'

This equation would hold good for a reaction of the type:



If a large concentration of hydrogen is used, the change in its concentration is small, and therefore its concentration is assumed to remain

constant.

For a particular catalyst, the factor Z may also be taken as a constant and can be combined with the factor k_1 to form a new rate constant k_2 . Since the products of reaction are analyzed for nitrogen, and the feedstock is based on nitrogen concentration, it is advisable to base our reaction on the concentration of nitrogen rather than on a particular nitrogen compound. This changes our equation to the new form:

$$r = \frac{-dC_N}{dt} = k_2 C_N^n \quad \text{-----} (4)$$

Since the amount of nitrogen remaining in the product is determined, we can rewrite the rate equation in terms of the initial concentration C_0 , and the amount converted, x :

$$r = \frac{dx}{dt} = k_2 (C_0 - x)^n \quad \text{-----} (5)$$

As the actual reaction time is virtually impossible to determine, we use an empirical time relation -- the space velocity (SV). The space velocity is defined as the ratio: volume feed per hour to volume catalyst. As such, it has the dimensions of reciprocal time. Rearranging equation (5), we obtain:

$$\int_0^x \frac{dx}{(C_0 - x)^n} = \frac{k'}{SV} \quad \text{-----} (6)$$

The order of the reaction is then equal to the exponent, n , in equation (6). For the case of a first order reaction where $n = 1$:

$$\int_0^x \frac{dx}{(C_0 - x)} = \frac{k'}{SV} \quad \text{-----}(7)$$

This integrates to:

$$\ln\left(\frac{C_0}{C_0 - x}\right) = \frac{k'}{SV} \quad \text{-----}(8)$$

A plot of $\ln(C_0/C_0 - x)$ against $1/SV$ would then yield a straight line with a slope k' and an intercept of zero.

For a reaction order of 2, the following should be plotted and the results examined to determine whether the data fits a straight line:

Plot $1/(C_0 - x)$ against $1/SV$, the intercept
will be $1/C_0$.

The common method of determining the value of n is to assume different orders of reaction until one is found that fits the data well.

B. Regression Analysis to Determine Fit of Proposed Reaction Order

The experimental data for most of the compounds run consisted of three pairs of observations. The following mathematical model was applied to the data and an analysis of variance table was constructed for each set of runs.

Mathematical Model: General Case;

$$Y_{1j} = \beta X_i + \epsilon_{1j} \quad i = 1, 2, \dots, K$$

$$\epsilon_{1j} \text{ are NID}(0, \sigma^2) \quad j = 1, 2, \dots, N$$

For the five member ring compounds:

$$Y_{1j} = (1/(C_0 - x) - 1/C_0)_{1j} \quad \text{and} \quad X_1 = (1/S.V.)_1$$

For the six member ring compounds:

$$Y_{1j} = (\ln C_0 / (C_0 - x))_{1j} \quad \text{and} \quad X_1 = (1/S.V.)_1$$

The maximum likelihood estimator of β is:

$$b = \frac{1}{N} \frac{\sum_{i=1}^K Y_i \cdot X_i}{\sum_{i=1}^K X_i^2} = \frac{\sum_{i=1}^K \bar{Y}_i X_i}{\sum_{i=1}^K X_i^2}$$

where

$$\bar{Y}_i = \frac{1}{N} \sum_{j=1}^N Y_{1j} = \frac{1}{N} Y_i$$

"Variance of b"

$$\text{Var.}(b) = \frac{1}{N} \frac{\sigma^2}{\sum_{i=1}^K X_i^2}$$

The appropriate analysis of variance based on the following partition of

the 'total' sum of squares: $\sum_{i=1}^K \sum_{j=1}^N Y_{1j}^2$

$$\text{Partition: } \sum_{i=1}^K \sum_{j=1}^N Y_{1j}^2 = Nb^2 \sum_{i=1}^K X_i^2 + N \sum_{i=1}^K (\bar{Y}_i - bX_i)^2 +$$

$$\sum_{i=1}^K \sum_{j=1}^N (Y_{1j} - \bar{Y}_i)^2 =$$

S.S.R. + S.S.D.R. + S.S.E.

where

$$S.S.R. = Nb^2 \sum_{i=1}^K X_i^2$$

$$S.S.D.R. = N \sum_{i=1}^K (\bar{Y}_i - bX_i)^2$$

$$S.S.E. = \sum_{i=1}^K \sum_{j=1}^N (Y_{ij} - \bar{Y}_i)^2$$

Analysis of Variance:

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Expected Mean Square
Regression	S.S.R.	1	s s r	$\sigma^2 + N\beta^2 \sum_{i=1}^K X_i^2$
Deviations from Regression	S.S.D.R.	K-1	s s d r	σ^2
Error	S.S.E.	K(N-1)	s s e	σ^2
Total	$\sum_{ij} Y_{ij}^2$	KN	---	---

To test the hypothesis of linearity we compute the F ratio:

$$F \text{ calculated} = \frac{ssdr}{sse}$$

and we compare this ratio with $F_{\alpha}(K-1, K(N-1))$

Should F calculated exceed $F_{\alpha}(K-1, K(N-1))$, we reject the hypothesis that the experimental data fit a line passing through the origin as derived from simple kinetic theory.

Confidence Interval Estimates for the Regression Coefficients:

Should we accept the hypothesis that the linear model fits the data, we are in a position to place confidence intervals on our regression coefficient, b , the slope of the regression line that is interpreted as the reaction rate constant.

L_1 and L_2 are defined as:

$$L_1 = b + t_{\alpha(K(N-1))} \cdot S_b$$

$$L_2 = b - t_{\alpha(K(N-1))} \cdot S_b$$

where

$$S_b^2 = \frac{S_E^2}{N \sum_{i=1}^K X_i^2}$$

and

$$S_E^2 = s.s.e$$

C. Multiple Regression

When data cannot be fitted to the more common methods of analysis such as have just been described in the last section, it is often necessary and useful to resort to other methods of analysis. One of the most important of these methods is that of multiple regression (4, 10, 15).

In using multiple regression, we assume that some random observation Y is expressible as a function of some independent, known variables $X_1, X_2, \dots, X_k$, say, with an error term e_i which is normally and independently distributed about a mean of zero with a variance σ^2 ; e.g., $\sum_i$ are NID(0, σ^2).

In this study, the observed value Y was the conversion and it was expressed as both linear and quadratic functions of the process variables space velocity and initial nitrogen concentration.

The model used under the linear assumption is:

$$Y_i = B_0 + B_1X_{1i} + B_2X_{2i} + e_i \quad \text{----- (9)}$$

where Y_i is the percentage conversion at the i^{th} level, X_{1i} the initial concentration, and X_{2i} the space velocity, and the $\sum_{i=1}^n e_i$ are $NID(0, \sigma^2)$.

This particular assumption is noted to be inconsistent with the assumption made when construction the analysis of variance tables for the experimental data.

In the latter case, the Y_{ij} term was a logarithmic function of x , the amount converted, and in both cases we have assumed the parameter to be normally and independently distributed. However, in this study, as the two models are being used for two dissimilar purposes, we feel justified in their use.

To estimate the B 's and σ^2 in the above model, we use the method of maximum likelihood (4). The likelihood function is:

$$L = \left(\frac{1}{2\pi\sigma^2} \right)^{n/2} \exp \left(- \frac{1}{2\sigma^2} \sum_{i=1}^n (Y_i - B_0 - B_1X_{1i} - B_2X_{2i})^2 \right)$$

The maximum likelihood estimators of the B 's and σ^2 are those estimators that maximize $\ln L$ for given observed Y 's and fixed X 's. These estimators

are found by taking the partial derivatives of $\ln L$ with respect to B_0 , B_1 , B_2 and σ^2 and equating these partials to zero. Those values of B_0 , B_1 , B_2 , and σ^2 which satisfy the equations thus obtained are said to be the maximum likelihood estimators of the above parameters. These estimators are denoted by b_0 , b_1 , b_2 , and $\hat{\sigma}^2$, respectively. Performing the above work on the estimating equations yields the desired estimates of the parameters.

This procedure was done for both the linear and quadratic models and the estimators obtained. The actual calculations were handled by the IBM 1620 computer available at Montana State College.

Certain statistical hypotheses were tested regarding the models used. Wherever possible, tests of these hypotheses were made and an analysis of variance table constructed.

V DISCUSSION OF RESULTS

A. Introduction:

Previous experience in the field of hydrodenitrogenation has shown that a second order reaction holds reasonably well for pyrrole, a five member ring compound, at temperatures from 675-725°F and a pressure of 250 psig (17).

Quinoline and pyridine, both six member ring compounds, were shown to follow a first order rate equation (16, 17) under similar operating conditions.

It was therefore reasonable to examine the data obtained in this study to see whether five member ring compounds followed second order rate equations and six member ring compounds followed first order rate equations.

B. Rate Equations - Five Member Ring Compounds:

Six five member ring compounds were run in this study. Carbazole was not run as it proved to be insoluble in toluene. The data from these runs are given in Table II.

A plot of $1/(C_0-x)$ vs. $1/SV$ will yield a straight line if the reaction is of second order. Plots of $1/(C_0-x)$ vs. $1/SV$ are shown in Figures 3 and 4 for all these compounds. Analysis of variance tables were constructed from the experimental data to test the hypothesis that the lines obtained from the plots were linear. Tables III-1 through III-9 are the analysis of variance tables for the five member ring compounds run.

It appeared that the experimental data fitted the assumption of a second order reaction except for pyrrole at 0.3 weight percent nitrogen.

Second order rate constants were calculated by the method of least squares (15) and 95 percent confidence interval estimates were placed on the rate constants obtained. These results are tabulated in Table IV.

As insufficient data was obtained for indole, the rate constant is given without a confidence interval.

Two five member ring compounds, pyrrole and pyrrolidine, were also studied at concentrations of 1.0 wt. percent and 2.5 wt. percent nitrogen. The data from these runs is also listed in Table IV. At both higher concentration levels, second order reactions were found to hold. Figures 5 and 6 are plots showing the effect of initial concentration on the reaction rate constant of these compounds. It can be seen that the reaction rate constant decreased rapidly as the initial concentration increased. A better representation of this effect is given in Figure 7 in which the reaction rate constant is plotted against the initial concentration. Thus, it can be seen that the reaction rate remains second order but the reaction rate constant decreases for higher initial nitrogen concentration.

The effect of substituting radicals for a hydrogen atom in the normal position, i.e., on the nitrogen atom in the ring, can also be seen from Table IV. With reference to pyrrolidine, it may be noted:

k (Pyrrolidine)	=	63.05
k (N-Methyl Pyrrolidine)	=	25.50
k (N-Butylene Pyrrolidine)	=	42.63

The rate constant is decreased considerably by this substitution.

C. Rate Equations - Six Member Ring Compounds:

Twenty-two six member ring nitrogen compounds were investigated in this study. The experimental data from the runs on these compounds are given in Table V and are plotted on Figures 8 through 13.

First order rate equations were assumed to apply in the case of six member ring compounds and thus the data were plotted as $\ln (C_0/C_0-x)$ vs. $1/SV$. A plot of this type will yield a straight line passing through the origin if the reaction is of first order.

Analysis of Variance Tables: Tables VI-1 through VI-19 were constructed from the experimental data to test the hypothesis that the lines obtained from the plotted data were linear and passed through the origin.

It appeared that the experimental data fitted the first order reaction assumed except in the cases of piperazine and 4-benzyl pyridine.

First order rate constants were calculated by the method of least squares (15) and 95 percent confidence interval estimates were placed on the rate constants obtained. These results are tabulated in Table VII.

Insufficient data points were obtained for the following compounds:

4-Ethyl-Pyridine, 4-Isopropyl-Pyridine, 3-4-Lutidine, 3-5-Lutidine,

2,4,6-Collidine, Quinoline and Acridine. No attempt was, therefore, made at constructing analysis of variance tables or placing confidence interval estimates on the rate constants obtained for these compounds.

Three groups of mono-substituted isomers of pyridine were included in the group of heterocyclics studied. These were the methyl pyridines (picolines), the ethyl pyridines, and the benzyl pyridines. The boiling points for the compounds in these three groups were noted to be a direct function of the position of the substituted radical, the further removed from the nitrogen atom the substituted radical is, the higher the boiling point. Reaction rate constants for these compounds have a reverse relationship. The further removed the substituted radical, the lower was the rate constant obtained. Table VIII shows these findings. The reaction rate constants of these compounds were plotted against their boiling points in Figure 14. It can be seen that for groups of isomers, the boiling point is inversely correlated with the reaction rate constant. The higher the boiling point, the lower is the reaction rate constant. Note, too, that the lines joining the points of each group have much the same slope. Thus the reaction rate constants for a group of pyridine isomers may be correlated with the boiling points of the isomers using the following relation:

$$k = a + bT$$

where k is the reaction rate constant,

a is a constant for a particular group of isomers,

b is the slope of the plots,

T is the normal boiling point of the isomers, °C.

The slopes of the plots were obtained and the average slope is -0.0870; thus the value of b is -0.0870.

A single group of di-substituted isomers was investigated. These were the lutidines or di-methyl pyridines. The reaction rate constants were again found to be a function of the boiling points of the compounds in this group. The lower the boiling point, the higher was the reaction rate constant and the greater the ease of denitrogenation. Table IX illustrates these findings. Again, the rate constants were plotted against the boiling points of these compounds. The results are also plotted on Figure 14 for comparison purposes with the results obtained for the mono-substituted pyridines. It can be seen that the same functional relation that held good for the mono-substituted pyridines also holds good for the di-substituted pyridines, the slope of the plot for the lutidines being: -0.0826.

Thus it can be seen that if the boiling point and the reaction rate constant are known for a pyridine isomer, it is possible to predict the value of the reaction rate constant for another isomer by knowledge of the second isomer's boiling point. This naturally holds for denitrogenation under identical operating conditions.

Two six member ring compounds, pyridine and 2,6-lutidine, were studied at concentrations of 1.0 Wt.% and 2.5 Wt.% nitrogen. The data from these runs are listed in Table V. Figures 15 and 16 are plots of

$\ln(C_0/C_{0-x})$ vs. $1/SV$ for these compounds at the different concentrations. It can be seen from these two plots that the rate constant decreases with initial nitrogen concentration as in the case of the five member ring compounds, pyrrole and pyrrolidine. Note, however, that the first order rate equation correlates the data extremely well at all concentrations investigated. Figure 17 is a plot of the first order rate constants obtained from the above plots vs. the initial nitrogen concentration. Again, it can be seen that the shape of the curves is very similar to those in Figure 7. Hence, as the initial nitrogen concentration is increased, the reaction rate constant decreases.

D. Comparison of Reaction Rates, Saturated and Unsaturated Compounds:

Table X lists the rates of reaction, both first and second order for some unsaturated and saturated heterocyclic nitrogen compounds.

In all cases the reaction rate constants for the saturated compounds are greater than those for the unsaturated compounds. Hence, saturated compounds are easier to denitrogenate than unsaturated compounds. A theoretical reason for this is that the saturated compounds possess lower bond energies than the unsaturated ones, thus making it easier for the compounds to hydrogenate. Also, it must be remembered that before the unsaturated compounds hydrogenate to straight chain hydrocarbons, they must first hydrogenate to the saturated heterocyclics. This effect has been reported in the literature (9, 16).

E. Multiple Regression of Percentage Conversion on Initial Concentration and Space Velocity:

The data obtained from the concentration runs were used in the estimation of the parameters of the linear and quadratic models that have previously been postulated. Hypotheses concerning these models were also tested using the data. The nomenclature adopted was as follows:

Y - Percentage Nitrogen Conversion, $100 \cdot x/C_0$

X_1 - Initial Nitrogen Concentration, C_0

X_2 - Space Velocity, $v/v/hr$ (SV)

Two models were postulated for the regression of the percentage nitrogen conversion, Y , on the variables, initial nitrogen concentration, X_1 , and space velocity, X_2 .

The linear model used was:

$$Y_1 = B_0 + B_1X_{11} + B_2X_{21} + e_1 \quad \text{-----}(10)$$

and the corresponding quadratic model was:

$$Y_1 = B_0 + B_1X_{11} + B_2X_{21} + B_{11}X_{11}^2 + B_{22}X_{21}^2 + B_{12}X_{11}X_{21} + e_1 \quad \text{-----}(11)$$

These two models were tested using the concentration run data for two five member ring compounds, pyrrole and pyrrolidine. The data for the regression analysis are given in Table II. Two six member ring compounds, pyridine and 2,6-lutidine, were also analyzed in this manner and the data for these compounds are given in Table V.

The regression coefficients, (B's) were estimated by the method of maximum likelihood that has been mentioned previously, the actual calculations being done on the IBM 1620 computer. The regression coefficients for the linear model were listed in Table XI. Note that the B_0 's are all in the neighborhood of 100. This indicates that at zero initial nitrogen concentration and space velocity, the conversion would be 100%, which is as expected.

A sample calculation is performed below to illustrate the use of these regression equations:

For example, pyrrole,

$$X_1 = 0.966 \text{ Wt.\% N}$$

$$X_2 = 1.0 \text{ (SV)}$$

$$\hat{Y} = 99.814217 - 23692417X_1 - 4.6123156X_2 = 72.30$$

where $\hat{Y}$ is the estimator of Y .

The conversion from this equation is 72.3%. From Table II, the observed conversion is 72.7%. Thus, it can be seen that in this case the regression equation estimates the conversion with extremely good accuracy.

Another parameter that gives an idea of the 'goodness of fit' of regression equations is the coefficient of multiple correlation, R^2 . These are listed for the linear models in Table XVI. The coefficient of multiple correlation can range zero to one; generally speaking, a correlation coefficient of 0.64 or greater is considered an indication that the regression equation postulated fits the data well. Table XVI shows that the smallest correlation coefficient obtained from the linear

models is 0.8095 for 2,6-lutidine. Thus, it appears that the linear models are fairly good representations of the function governing yield.

Certain statistical hypotheses about the above models can be tested. These hypotheses include:

for the linear model, $H : B_1 = B_2 = 0$

and for the quadratic model, $H : B_{11} = B_{22} = B_{12} = 0$

The hypothesis: $B_1 = B_2 = 0$ was tested for the four linear models and in each case the hypothesis was rejected. The analysis of variance tables for the four compounds are given in Tables XI - XIV in the Appendix. This implies that both the initial nitrogen concentration and the space velocity affect the percentage conversion obtained. This conclusion can almost be deduced from looking at the data.

The regression coefficients for the quadratic model are tabulated in Table XVII. Note again that the B_0 's are in the neighborhood of 100. A sample calculation for the same case as previously illustrated is given below:

For example, pyrrole, $X_1 = 0.966$ Wt.% N

$X_2 = 1.0$ (SV)

$$\hat{Y} = 103.4699 - 42.499924X_1 - 1.4676398X_2 + 5.0149852X_1^2 + 0.009507762X_2^2 - 0.00284890X_1X_2$$

$$\hat{Y} = 66.56.$$

The conversion obtained from this equation is 66.56%. From Table II, the actual percentage conversion is 72.7%. Thus, it is seen that in the example chosen, the linear model seems to be a better estimator than does

the quadratic model. However, one must bear in mind that this is not so for the majority of the data in which the quadratic model is the better estimator. This fact is borne out by observing the coefficient of multiple correlation for the quadratic models and comparing them with those obtained for the linear models. The correlation coefficients for the quadratic models are tabulated in Table XXII. The lowest correlation coefficient was obtained in the case of 2,6-lutidine as before, but the correlation coefficient is 0.9687 with a maximum correlation coefficient of 0.9891 for pyridine. Contrast these with the values of 0.8095 obtained for 2,6-lutidine and 0.8387 for pyridine from the linear models and it can be clearly seen that the quadratic model is a better estimator than the linear model for all compounds tested.

The other series of hypotheses tested were those for the quadratic models, $H: B_{11} = B_{22} = B_{12} = 0$. To do this, we tested for the reduction in sums of squares for error due to fitting to the quadratic term after fitting to the linear term. The degrees of freedom used in this test were three, since there are three quadratic terms. From the results of these tests we can decide whether the quadratic terms are significant in predicting conversions. The analysis of variance tables for these models are given in Tables XVIII - XXI. In all cases the above hypotheses were rejected. It is, therefore, concluded that the quadratic terms and the interaction term are significant and that the quadratic models are better estimators of the data than the linear models.

A final means of interpreting the quadratic regression equation obtained is to eliminate the cross products term and obtain the canonical equation of the type:

$$Y - Y_s = \lambda_1 Z_1^2 + \lambda_2 Z_2^2$$

where Z_1, Z_2 are some new transformed variables, in order to determine the optimum conditions (15).

To calculate Y_s , the stationary point, it is first necessary to calculate X_{1s} and X_{2s} . This is done by taking the partial derivatives of the quadratic regression equation with respect to X_1 and X_2 and equating to zero. The following results were then obtained:

<u>Compound</u>	<u>X_{1s}</u>	<u>X_{2s}</u>	<u>Y_s</u>
Pyrrole	4.225	82.60	-44.24
Pyrrolidine	3.37	342.0	-12.43
Pyridine	3.01	11.23	-26.72
2,6-Lutidine	3.55	11.66	-22.67

The results show that the stationary point is not within the range investigated; thus, further work was deemed unnecessary.

A contour plot of the conversion obtained on the X_1 and X_2 axes is shown for pyrrole in Figure 18. From this plot it is apparent that the optimum point is at origin, $X_1 = 0$, and $X_2 = 0$; as operating conditions move outward from the origin, the percentage conversion decreases.

VI CONCLUSIONS

The destructive catalytic hydrogenation for five member heterocyclic nitrogen compounds appears to be of second order, while that of six member heterocyclic nitrogen compounds appears to be of first order.

A methyl group or other radical substituted into the normal position, i.e., onto the nitrogen atom in five member ring heterocyclics, greatly reduces the reaction rate constant. This substitution must strengthen the ring making it less susceptible to hydrogenation.

Concentration studies on both five and six member ring heterocyclic nitrogen compounds showed that as the initial nitrogen concentration was increased, the reaction rate constant decreased under the same operating conditions. No simple relationship between conversion and initial conversion was observed.

Multiple regression of the percentage conversion on the initial concentration and space velocity indicates that the percentage conversion may be predicted fairly well by a linear model for the four compounds pyrrole, pyrrolidine, pyridine, and 2,6-lutidine. Correlation coefficients for the linear regression were high, ranging from 0.80 to 0.91. It was also found that the percentage conversion could also be predicted by a quadratic model using the same variables as before. The quadratic model gave a slightly better fit of the data, correlation coefficients from 0.96 to 0.98 being obtained.

First order reaction rate constants for three groups of mono-substituted isomers of pyridine and one group of di-substituted isomers of pyridine were found to correlate with the boiling points of the isomers. A relation of the type $k = a + bT$ was obtained from the data, where $b_{\text{average}} = -0.0848$.

Finally, the reaction rate constants of both five member and six member ring saturated and unsaturated compounds were compared. The reaction rates for the unsaturated nitrogen heterocyclics were found in all cases to be greater than those for the saturated nitrogen heterocyclics. The reason for this effect seems to be the fact that unsaturated compounds first hydrogenate to the saturated compound before further hydrogenating to a straight chain hydrocarbon and ammonia.

The calculations and observations leading to the above conclusions were all based on the overall nitrogen concentration, and all runs for comparison purposes were performed under similar operating conditions as far as possible.

Further studies along these lines should be done on feed mixtures containing mixtures of compounds. A feed composed of two nitrogen compounds, one with a high reaction rate constant and another with a low reaction rate constant could be run in order to see whether the feed would selectively denitrogenate, thus enabling one of the two compounds to be recovered.

Work should also be done on the destructive catalytic hydrogenation of commercial feed stocks that contain nitrogen compounds. If the nitrogen compounds that are in this feed stock could be recognized as being similar to some of the compounds used in this study, an idea of the ease or difficulty of removing these compounds from the feed stock in question may be gained by reference to some of the results presented in this thesis.

VII ACKNOWLEDGEMENT

The author would like to acknowledge the financial assistance of the Engineering Experiment Station of Montana State College which made this project possible.

He would like to thank the members of the staff of the Chemical Engineering Department for their comments and careful criticisms during the course of this research, and in particular, Dr. Lloyd Berg, who directed this research project.

He also wishes to thank Dr. Charles Mode and Dr. Frank McFeely of the Mathematics Department, who lent some of their time in personal consultation, and the staff of the Computer Laboratory, in particular Mr. L. Amunrud, who helped the author with the computation of the regression equation on the IBM 1620 computer.

VIII LITERATURE CITED.

- (1) Ball, J. S., et al., "Composition of Colorado Shale-Oil Naphtha", Ind. and Eng. Chem., 41:581 (1949)
- (2) Ball, J. S., et al., "Nitrogen Content of Crude Petroleum", Ind. and Eng. Chem., 43:25 (1951)
- (3) Berg, Clyde, "Refining of High Sulfur Stocks by the Cobalt-Molybdate Process", Proceedings, Athabasca Oil Sands Conference, (September 1961), Government of Alberta, Edmonton, Canada.
- (4) Brunk, H. D., "An Introduction to Mathematical Statistics", Ginn and Company, New York, (1960)
- (5) Currie, R. A., M.S. Thesis, Montana State College, (1960)
- (6) Glasstone, S., "Thermodynamics for Chemists", D. Van Nostrand Company, Inc., New York, (1947)
- (7) Hirst, L. L., and C. C. Chafee, "Liquid Fuel from Coal", Ind. and Eng. Chem., 42:1607 (1950)
- (8) Hodgeman, C. D., and H. N. Holmes, "Handbook of Chemistry and Physics", The Chemical Rubber Publishing Company, Cleveland, Ohio, (1953)
- (9) Karrer, Paul, "Organic Chemistry". The Elsevier Publishing Company, Inc., New York. (1950)
- (10) Kempthorne, Oscar, "The Design and Analysis of Experiments", John Wiley and Sons, Inc., New York, (1952)
- (11) Kirk, P. L., "Kjeldahl Method for Total Nitrogen", Anal. Chem., 22:354 (1950)
- (12) Mahugh, R. A., Ph.D. Thesis, Montana State College, (1960)
- (13) McKee, A. F., M.S. Thesis, Montana State College, (1956)
- (14) Mills, G. A., et al., "Chemical Characteristics of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ions." J. Amer. Chem. Soc., 72:1544 (1950)

- (15) Ostle, B., "Statistics in Research", Iowa State College Press, Ames, Iowa, (1954)
- (16) Ryffel, J. R., Ph.D. Thesis, Montana State College, (1960)
- (17) Schreiber, G. P., Ph.D. Thesis, Montana State College, (1961)
- (18) Smith, J. M., "Chemical Engineering Kinetics", McGraw-Hill Book Company, New York, (1956)
- (19) Staff Report, "Carbide Takes the Hex Out of Coal", Chem. Eng. News, 30:1954 (1952)

IX APPENDIX

	Page
Table I Heterocyclic Nitrogen Compounds Used in This Study -----	46
Table II Reaction Rate and Multiple Regression Data for Five Member Ring Compounds -----	47
Table III-1 Analysis of Variance Tables for Five Member Ring Compounds -----	49
to III-9	53
Table IV Reaction Rate Constants at 700°F for Five Member Ring Compounds -----	53
Table V Reaction Rate and Multiple Regression Data for Six Member Ring Compounds -----	54
Table VI-1 Analysis of Variance Tables for Six Member Ring Compounds -----	59
to VI-19	68
Table VII Reaction Rate Constants at 700°F for Six Member Ring Compounds -----	69
Table VIII Boiling Points and Reaction Rate Constants for Mon-Substituted Pyridine Compounds -----	70
Table IX Boiling Points and Reaction Rate Constants for Di-Substituted Pyridine Compounds -----	70
Table X Comparison of Reaction Rate Constants for Saturated and Unsaturated Heterocyclic Nitrogen Compounds -----	71
Table XI Estimated Coefficients for Regression--- Linear Model -----	71
Table XII Analysis of Variance Table for Pyrrole-- Linear Model -----	72
Table XIII Analysis of Variance Table for Pyrrolidine-- Linear Model -----	73
Table XIV Analysis of Variance Table for Pyridine-- Linear Model -----	73

Table XV	Analysis of Variance Table for 2,6-Lutidine-- Linear Model -----	74
Table XVI	Coefficients of Multiple Regression-- Linear Models -----	74
Table XVII	Estimated Coefficients for Regression-- Quadratic Model -----	75
Table XVIII	Analysis of Variance Table for Pyrrole-- Quadratic Model -----	76
Table XIX	Analysis of Variance Table for Pyrrolidine-- Quadratic Model -----	76
Table XX	Analysis of Variance Table for Pyridine-- Quadratic Model -----	77
Table XXI	Analysis of Variance Table for 2,6-Lutidine-- Quadratic Model -----	77
Table XXII	Coefficients of Multiple Regression-- Quadratic Models -----	78
Figure 1	Schematic Flow Diagram -----	79
Figure 2	Detailed Diagram of Reactor -----	80
Figure 3	Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity -----	81
Figure 4	Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity for Five Member Ring Compounds -----	82
Figure 5	Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity for Pyrrole 0.3, 1.0, 2.5 Wt.% N. -----	83
Figure 6	Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity for Pyrrolidine 0.3, 1.0, 2.5 Wt.% N. -----	84
Figure 7	Reaction Rate Constant vs. Initial Nitrogen Concentration for Pyrrole and Pyrrolidine -----	85
Figure 8	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 100-140°C. -----	86

Figure 9	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 100-140°C. -----	87
Figure 10	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 140-170°C. -----	88
Figure 11	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 140-170°C. -----	89
Figure 12	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 170-350°C. -----	90
Figure 13	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds, Boiling Point Range: 170-350°C. -----	91
Figure 14	Plot of Boiling Points vs. Reaction Rate Constants for the Mono- and the Di-Substituted Pyridines. -----	92
Figure 15	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Pyridine: 0.3, 1.0, 2.2 Wt.% N. -----	93
Figure 16	Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for 2,6-Lutidine: 0.3, 1.0, 2.45 Wt.% N. -----	94
Figure 17	Reaction Rate Constants vs. Initial Nitrogen Concentration for Pyridine and 2,6-Lutidine. -----	95
Figure 18	Plot of Percentage Conversion Contour Surface for Pyrrole. -----	96
Curriculum Vita -----		97

TABLE I

HETEROCYCLIC NITROGEN COMPOUNDS USED IN THIS STUDY

<u>Compound</u>	<u>MW</u>	<u>BP (°C)</u> <u>760 mm</u>	<u>State</u>	<u>Source</u>
<u>Five Member Ring Compounds:</u>				
Pyrrole	67.1	131	L	Ansul Chem. Co.
N-Methyl Pyrrole	81.1	112	L	Ansul Chem. Co.
Pyrrolidine	71.1	88	L	Dist. Prod. Ind.
N-Methyl Pyrrolidine	85.15	80.5	L	Ansul Chem. Co.
N-Butylene Pyrrolidine	125.21	154	L	Ansul Chem. Co.
Indole	117.14	253	L	Dist. Prod. Ind.
Carbazole	167.2	355	S	Dist. Prod. Ind.
<u>Six Member Ring Compounds:</u>				
Pyrazine	80.09	118	S	Wyandotte Chem. Co.
Pyridine	79.10	115.5	L	Ansul Chem. Co.
2-Picoline	93.12	128.8	L	Dist. Prod. Ind.
3-Picoline	93.12	143.5	L	Dist. Prod. Ind.
4-Picoline	93.12	143.1	L	Dist. Prod. Ind.
2-Ethyl Pyridine	107.15	148	L	Reilly Tar & Chem. Corp.
4-Ethyl Pyridine	107.15	166	L	Reilly Tar & Chem. Corp.
4-Isopropyl Pyridine	122.15	182	L	Reilly Tar, etc.
2-Benzyl Pyridine	169.22	276	L	Reilly Tar, etc.
4-Benzyl Pyridine	169.22	287	L	Reilly Tar, etc.
2,4-Lutidine	107.16	158	L	Dist. Prod. Ind.
2,6-Lutidine	107.16	142.5	L	Dist. Prod. Ind.
3,4-Lutidine	107.16	164	L	Dist. Prod. Ind.
3,5-Lutidine	107.16	---	L	Reilly Tar, etc.
3-Ethyl-4-Methyl Pyridine	121.18	195	L	Aldrich Chem. Co.
2,4,6-Collidine	121.18	171.5	L	Reilly Tar, etc.
Piperazine	86.13	145.5	S	Dist. Prod. Ind.
Piperidine	85.15	106	L	Dist. Prod. Ind.
2-Methyl Piperidine	99.17	125.5	L	Reilly Tar, etc.
2,6-Dimethyl Piperidine	113	126.5	L	Reilly Tar, etc.
Quinoline	129.15	237.1	L	Barrett Chem. Co.
Acridine	179.21	346	S	Dist. Prod. Ind.

TABLE II

REACTION RATE AND MULTIPLE REGRESSION DATA FOR FIVE MEMBER RING COMPOUNDS

Compound	S.V.	C_0	C_0-x	C_0-x/C_0	$1/C_0-x$	$100x/C_0$
Pyrrole	10.0	0.313	0.1710	0.545	5.85	45.5
	10.0	0.313	0.1610	0.515	6.20	48.5
	4.0	0.335	0.0682	0.204	14.65	79.6
	4.0	0.335	0.0695	0.2075	14.40	79.25
	2.0	0.335	0.0294	0.0878	34.0	91.2
	2.0	0.335	0.0285	0.0852	35.2	91.5
	4.0	0.966	0.496	0.513	2.02	48.7
	4.0	0.966	0.548	0.556	1.82	44.4
	2.0	0.966	0.398	0.412	2.51	58.8
	2.0	0.966	0.398	0.412	2.51	58.8
	1.0	0.966	0.264	0.273	3.79	72.7
	1.0	0.966	0.298	0.309	3.36	69.1
	4.0	2.57	2.043	0.798	0.488	20.2
	4.0	2.57	1.990	0.775	0.502	22.5
	2.0	2.57	1.776	0.690	0.553	31.0
	2.0	2.57	1.788	0.695	0.560	30.5
	1.0	2.57	1.514	0.590	0.650	41.0
	1.0	2.57	1.368	0.532	0.731	46.8
N-Methyl Pyrrole	4.0	0.303	0.2005	0.663	5.00	33.7
	4.0	0.303	0.207	0.674	4.83	32.6
	2.0	0.3045	0.1147	0.376	8.72	62.4
	2.0	0.3045	0.120	0.394	8.34	60.6
	1.0	0.316	0.0838	0.264	11.90	73.6
	1.0	0.316	0.0687	0.218	14.50	78.2
Pyrrolidine	20.0	0.3175	0.178	0.561	5.62	43.9
	20.0	0.3175	0.1835	0.577	5.45	42.3
	10.0	0.315	0.102	0.324	9.8	67.6
	10.0	0.315	0.1075	0.341	9.3	65.9
	4.0	0.3485	0.0522	0.150	19.2	85.0
	4.0	0.3485	0.0545	0.156	18.4	84.6
	20.0	0.976	0.748	0.756	1.335	24.4
	20.0	0.976	0.7505	0.758	1.331	24.2
	10.0	0.976	0.642	0.657	1.560	34.3
	10.0	0.976	0.612	0.626	1.633	37.4
	5.0	0.976	0.463	0.474	2.160	52.6
	5.0	0.976	0.463	0.474	2.160	52.6
	5.0	0.976	0.463	0.474	2.160	52.6

TABLE II -- continued

REACTION RATE AND MULTIPLE REGRESSION DATA FOR FIVE MEMBER RING COMPOUNDS

Compound	S.V.	C_0	C_0-x	C_0-x/C_0	$1/C_0-x$	$100x/C_0$
Pyrrolidine	20.0	2.290	2.093	0.913	0.478	8.7
	20.0	2.290	2.067	0.903	0.984	9.7
	10.0	2.290	1.819	0.795	0.550	20.5
	10.0	2.290	1.836	0.802	0.545	19.8
	5.0	2.290	1.706	0.745	0.586	25.5
	5.0	2.290	1.639	0.715	0.610	28.5
N-Methyl Pyrrolidine	10.0	0.293	0.1585	0.540	6.31	46.0
	10.0	0.293	0.171	0.584	5.84	41.6
	4.0	0.314	0.1345	0.429	7.55	57.1
	4.0	0.314	0.1205	0.385	8.30	61.5
	2.0	0.306	0.0585	0.191	17.1	80.9
	2.0	0.306	0.0608	0.198	16.5	80.2
N-Butylene Pyrrolidine	20.0	0.295	0.2315	0.785	4.32	21.5
	20.0	0.295	0.2235	0.758	4.47	24.2
	10.0	0.280	0.123	0.439	8.13	56.1
	10.0	0.280	0.115	0.410	8.70	59.0
	4.0	0.268	0.0252	0.0943	29.60	90.6
	4.0	0.268	0.0258	0.0961	28.8	90.4
Indole	4.0	0.290	0.259	0.893	3.86	10.7
	2.0	0.302	0.241	0.793	4.16	20.7
	1.0	0.287	0.172	0.600	5.81	40.0
	1.0	0.287	0.175	0.610	5.71	39.0

TABLE III

ANALYSIS OF VARIANCE TABLES -- FIVE MEMBER RING COMPOUNDS

Table III-1. Pyrrole 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	2232.551	1	2232.551
Deviations from Regression	47.331	2	23.665
Error	0.763	3	0.254
Total	2280.645	6	

$$F = 92.75 > F_{.05}(2,3) = 30.82$$

Reject H: Linearity

Table III-2. Pyrrole 1.0 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	19.2038	1	19.2038
Deviations from Regression	0.2429	2	0.1214
Error	0.1292	3	0.0431
Total	19.5759	6	

$$F = 2.82 < F_{.05}(2,3)$$

Accept H: Linearity

TABLE III -- continued

ANALYSIS OF VARIANCE TABLES --- FIVE MEMBER RING COMPOUNDS

Table III-3. Pyrrole 2.5 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.260229	1	0.260229
Deviations from Regression	0.002776	2	0.001388
Error	0.003313	3	0.001104
Total	0.266318	6	

$$F = 1.257 < F_{.05} (2,3)$$

Accept H: Linearity

Table III-4. N-Methyl Pyrrole
0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	258.6607	1	258.6607
Deviations from Regression	1.6808	2	0.8404
Error	3.4666	3	1.1555
Total	263.8081	6	

$$F = 0.73 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE III -- continued

ANALYSIS OF VARIANCE TABLES -- FIVE MEMBER RING COMPOUNDS

Table III-5. Pyrrolidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	596.295	1	596.295
Deviations from Regression	1.346	2	0.673
Error	0.460	3	0.153
Total	598.101	6	

$$F = 4.39 < F_{.05} (2,3)$$

Accept H: Linearity

Table III-6. Pyrrolidine 1.0 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	3.481228	1	3.481228
Deviations from Regression	0.00113	2	0.000565
Error	0.00587	3	0.001935
Total	3.42528	6	

$$F = 0.288 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE III -- continued

ANALYSIS OF VARIANCE TABLES -- FIVE MEMBER RING COMPOUNDS

Table III-7. Pyrrolidine 1.0 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.077313	1	0.077313
Deviations from Regression	0.001848	2	0.000924
Error	0.000119	3	0.000039
Total	0.079280	6	

$$F = 23.66 < F_{.05}(2,3)$$

Accept H: Linearity

Table III-8. N-Methyl Pyrrolidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	419.3586	1	419.3586
Deviations from Regression	6.5922	2	3.2961
Error	0.5673	3	0.1891
Total	426.5181	6	

$$F = 17.43 < F_{.05}(2,3)$$

Accept H: Linearity

TABLE III -- continued

ANALYSIS OF VARIANCE TABLES -- FIVE MEMBER RING COMPOUNDS

Table III-9. N-Butylene Pyrrolidine 0.3 Wt.% N.

Source of Variation	S.S.	d.f.	m.s.
Regression	272.5976	1	272.5976
Deviations from Regression	1.0059	2	0.5030
Error	0.5483	3	0.1813
Total	274.1518	6	

$$F = 2.774 \quad F_{.05} (2,3)$$

Accept H: Linearity

TABLE IV

REACTION RATE CONSTANTS, AT 700°F FOR FIVE MEMBER RING COMPOUNDS

Compound	C ₀	k(hr) ⁻¹ (Wt.% N) ⁻¹	95% Confidence Limits
Pyrrole	0.335	--- Non-Linear ---	
Pyrrole	0.966	2.82	± 0.418
Pyrrole	2.570	0.315	± 0.0655
N-Methyl Pyrrole	0.303	9.93	± 2.157
Pyrrolidine	0.3175	63.05	± 3.22
Pyrrolidine	0.976	5.706	± 0.435
Pyrrolidine	2.290	0.858	± 0.00613
N-Methyl Pyrrolidine 0.306		25.50	± 1.725
N-Butyl. Pyrrolidine 0.295		42.63	± 3.51
Indole	0.290	2.07	None

TABLE V

REACTION RATE AND MULTIPLE REGRESSION DATA FOR SIX MEMBER RING COMPOUNDS

Compound	S.V.	C_0	C_0-x	C_0/C_0-x	$\ln C_0/C_0-x$	$100x/C_0$
Pyrazine	25.0	0.305	0.1235	2.47	0.804	59.5
	25.0	0.305	0.1150	2.55	0.936	60.7
	10.0	0.3075	0.064	4.7	1.55	78.8
	10.0	0.3075	0.0803	3.73	1.32	73.2
	4.0	0.306	0.01225	25.0	3.22	96.0
	4.0	0.306	0.00900	34.0	3.53	97.06
Pyridine	4.0	0.342	0.0207	1.65	0.501	39.5
	4.0	0.342	0.2242	1.53	0.425	34.7
	2.0	0.350	0.1184	2.95	1.08	66.1
	2.0	0.350	0.1107	3.16	1.15	68.4
	1.0	0.343	0.0770	4.46	1.495	77.6
	1.0	0.343	0.0670	5.13	1.635	80.5
	4.0	0.980	0.883	1.110	0.1094	9.8
	4.0	0.980	0.878	1.115	0.1083	10.3
	2.0	0.980	0.7555	1.295	0.255	22.8
	2.0	0.980	0.731	1.340	0.293	25.4
	1.0	0.980	0.5335	1.820	0.599	45.0
	1.0	0.980	0.540	1.795	0.585	44.3
	4.0	2.210	2.105	1.05	0.0488	4.8
	4.0	2.210	2.121	1.042	0.041	4.0
	2.0	2.210	1.965	1.125	0.117	11.1
	2.0	2.210	1.99	1.110	0.104	9.9
	1.0	2.210	1.768	1.25	0.223	20.1
	1.0	2.210	1.797	1.23	0.207	18.7
2-Picoline	10.0	0.316	0.02655	1.19	0.174	16.0
	10.0	0.316	0.0263	1.20	0.182	16.7
	4.0	0.301	0.1524	1.975	0.6805	49.4
	4.0	0.301	0.1418	2.12	0.7537	53.0
	2.0	0.296	0.0798	3.70	1.308	73.0
	2.0	0.296	0.0787	3.76	1.324	73.4
3-Picoline	4.0	0.319	0.301	1.06	0.0583	5.6
	4.0	0.319	0.301	1.06	0.0583	5.6
	1.0	0.3185	0.129	2.47	0.904	59.5
	1.0	0.3185	0.1325	2.40	0.875	58.4
	0.5	0.315	0.012	26.20	3.25	96.2
	0.5	0.315	0.0125	25.20	3.22	96.0

TABLE V.-- continued

REACTION RATE AND MULTIPLE REGRESSION DATA FOR SIX MEMBER RING COMPOUNDS

Compound	S.V.	C_0	C_0-x	C_0/C_0-x	$\ln C_0/C_0-x$	$100x/C_0$
4-Picoline	4.0	0.308	0.312	1.05	0.049	4.5
	4.0	0.308	0.291	1.07	0.068	6.5
	2.0	0.306	0.261	1.17	0.157	14.5
	2.0	0.306	0.2645	1.155	0.144	13.4
	1.0	0.306	0.1420	2.15	0.765	53.5
	1.0	0.306	0.1283	2.38	0.867	58.0
2-Ethyl Pyridine	4.0	0.3015	0.2257	1.33	0.2852	24.9
	4.0	0.3015	0.231	1.30	0.2624	23.1
	2.0	0.300	0.1776	1.69	0.5247	40.9
	2.0	0.300	0.178	1.683	0.523	40.7
	1.0	0.300	0.142	2.11	0.747	51.0
	1.0	0.300	0.127	2.36	0.860	56.0
4-Ethyl Pyridine	2.0	0.296	0.2655	1.12	0.113	10.6
	2.0	0.296	0.260	1.14	0.131	12.3
	1.0	0.295	0.195	1.51	0.412	33.6
	1.0	0.295	0.179	1.64	0.494	39.0
4-Isopropyl Pyridine	4.0	0.3005	0.297	1.01	0.0099	1.0
	4.0	0.3005	0.300	1.01	0.01	1.0
	2.0	0.303	0.283	1.07	0.0676	6.5
	2.0	0.303	0.301	1.01	0.01	1.0
	1.0	0.3015	0.2655	1.135	0.127	11.9
	1.0	0.3015	0.265	1.14	0.131	12.2
2-Benzyl Pyridine	10.0	0.304	0.256	1.19	0.174	16.0
	10.0	0.304	0.263	1.16	0.148	14.0
	4.0	0.302	0.149	2.02	0.7031	50.5
	4.0	0.302	0.151	2.00	0.6932	50.0
	2.0	0.302	0.0828	3.65	1.295	71.8
	2.0	0.302	0.0839	3.60	1.281	72.2
4-Benzyl Pyridine	10.0	0.300	0.2845	1.05	0.0488	5.0
	10.0	0.300	0.289	1.04	0.039	3.7
	4.0	0.306	0.197	1.55	0.438	35.5
	4.0	0.306	0.192	1.59	0.464	37.0
	2.0	0.314	0.1536	2.04	0.713	51.0
	2.0	0.314	0.155	2.03	0.708	50.7

TABLE V -- continued

REACTION RATE AND MULTIPLE REGRESSION DATA FOR SIX MEMBER RING COMPOUNDS

Compound	S.V.	C ₀	C _{0-x}	C ₀ /C _{0-x}	ln C ₀ /C _{0-x}	100x/C ₀
2,4-Lutidine	4.0	0.308	0.2885	1.07	0.067	6.5
	4.0	0.308	0.285	1.082	0.077	7.5
	2.0	0.3045	0.275	1.12	0.1153	9.99
	2.0	0.3045	0.279	1.11	0.1113	9.9
	1.0	0.3045	0.2205	1.38	0.322	27.5
	1.0	0.3045	0.216	1.41	0.244	29.0
2,6-Lutidine	4.0	0.2955	0.2135	1.39	0.3293	28.0
	4.0	0.2955	0.2175	1.36	0.3075	26.5
	2.0	0.296	0.120	2.47	0.9042	59.5
	2.0	0.296	0.121	2.45	0.896	59.2
	1.0	0.301	0.0497	6.06	1.802	83.5
	1.0	0.301	0.0467	6.45	1.864	84.5
	4.0	1.000	0.833	1.20	0.182	16.7
	4.0	1.000	0.835	1.195	0.177	16.5
	2.0	1.000	0.732	1.37	0.314	26.8
	2.0	1.000	0.714	1.40	0.336	28.4
	1.0	1.000	0.521	1.92	0.652	47.9
	1.0	1.000	0.441	2.27	0.819	55.9
	4.0	2.45	2.14	1.143	0.133	13.0
	4.0	2.45	2.17	1.130	0.122	11.5
	2.0	2.45	1.905	1.285	0.2507	22.3
	2.0	2.45	1.922	1.272	0.2406	21.5
	1.0	2.45	1.529	1.603	0.4718	37.6
	1.0	2.45	1.470	1.666	0.5104	40.0
3,4-Lutidine	1.0	0.316	0.315	1.001	0.0009	0.1
	1.0	0.316	0.307	1.03	0.0295	2.9
	0.445	0.314	0.230	1.364	0.310	26.7
	0.445	0.314	0.218	1.440	0.365	30.5
3,5-Lutidine	1.0	0.291	0.218	1.335	0.285	25.0
	1.0	0.291	0.224	1.30	0.262	23.0
3-Ethyl, 4-Methyl Pyridine	4.0	0.3655	0.3335	1.095	0.091	8.8
	4.0	0.3655	0.3425	1.065	0.062	5.4
	2.0	0.3675	0.341	1.079	0.077	7.3
	2.0	0.3675	0.342	1.075	0.0705	7.0
	1.0	0.303	0.2775	1.095	0.091	8.8
	1.0	0.303	0.2745	1.104	0.115	9.4

TABLE V -- continued

REACTION RATE AND MULTIPLE REGRESSION DATA FOR SIX MEMBER RING COMPOUNDS

Compound	S.V.	C_0	C_0-x	C_0/C_0-x	$\ln C_0/C_0-x$	$100x/C_0$
2,4,6-Collidine	1.0	0.307	0.190	1.61	0.476	37.9
	1.0	0.307	0.180	1.70	0.531	41.2
	0.5	0.308	0.110	2.80	1.03	64.3
	0.5	0.308	0.110	2.80	1.03	64.3
Piperazine	20.0	0.312	0.0973	3.20	1.163	68.8
	20.0	0.312	0.098	3.18	1.157	68.6
	10.0	0.307	0.0410	7.49	2.0136	86.65
	10.0	0.307	0.0406	7.56	2.0229	86.8
	4.0	0.302	0.01	30.2	3.408	96.69
	4.0	0.302	0.0097	31.1	3.438	96.78
Piperidine	20.0	0.271	0.181	1.497	0.405	33.2
	20.0	0.271	0.189	1.434	0.360	30.4
	10.0	0.315	0.156	2.02	0.703	50.5
	10.0	0.315	0.160	1.97	0.678	49.3
	4.0	0.307	0.0378	8.12	2.094	87.7
	4.0	0.307	0.043	7.15	1.967	86.0
2-Methyl Piperidine	20.0	0.315	0.1735	1.815	0.598	45.0
	20.0	0.315	0.1802	1.75	0.560	43.0
	10.0	0.292	0.0562	5.20	1.649	80.8
	10.0	0.292	0.0569	5.14	1.637	80.5
	4.0	0.290	0.0305	9.52	2.253	89.5
	4.0	0.290	0.0292	9.94	2.297	90.0
2,6-Dimethyl Piperidine	10.0	0.295	0.0752	3.92	1.366	74.5
	10.0	0.295	0.0750	3.94	1.371	74.6
	4.0	0.302	0.0462	6.55	1.88	84.7
	4.0	0.302	0.0468	6.45	1.86	84.5
	2.0	0.3035	0.0228	13.3	3.496	92.5
	2.0	0.3035	0.0242	12.5	3.219	92.0
Quinoline	1.0	0.288	0.1955	1.472	0.386	32.1
	1.0	0.288	0.1985	1.45	0.372	31.0
	1.0	0.286	0.196	1.46	0.378	31.5
	1.0	0.286	0.196	1.46	0.378	31.5

TABLE V -- continued

REACTION RATE AND MULTIPLE REGRESSION DATA FOR SIX MEMBER RING COMPOUNDS

<u>Compound</u>	<u>S.V.</u>	<u>C₀</u>	<u>C₀-x</u>	<u>C₀/C₀-x</u>	<u>ln C₀/C₀-x</u>	<u>100x/C₀</u>
Acridine	4.0	0.3045	0.2875	1.06	0.058	5.7
	4.0	0.3045	0.302	1.01	0.01	1.0
	1.0	0.294	0.1715	0.715	0.5395	41.7
	1.0	0.294	0.240	1.225	0.1995	18.3
	0.5	0.2965	0.1923	1.54	0.4318	35.1
	0.5	0.2965	0.1922	1.54	0.4318	35.1

TABLE VI

ANALYSIS OF VARIANCE -- SIX MEMBER RING COMPOUNDS

Table VI-1. Pyrazine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	28.3317	1	28.3317
Deviations from Regression	0.0827	2	0.0413
Error	0.0823	3	0.0274
Total	28.4976	6	

$$F = 1.51 < F_{.05}(2,3) = 30.82$$

Accept H: :Linearity

Table VI-2. Pyridine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	9.05914	1	9.05914
Deviations from Regression	0.08600	2	0.04300
Error	0.03967	3	0.01322
Total	9.1848	6	

$$F = 3.253 < F_{.05}(2,3)$$

Accept H: :Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER RING COMPOUNDS

Table VI-3. Pyridine 1.0 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.871395	1	0.871395
Deviations from Regression	0.003372	2	0.00166
Error	0.00083	3	0.00027
Total	0.875597	6	

$$F = 6.26 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-4. Pyridine 2.5 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.120749	1	0.120749
Deviations from Regression	0.000171	2	0.000086
Error	0.000245	3	0.000082
Total	0.121165	6	

$$F = 1.05 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-5. 2-Picoline 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	4.53396	1	4.53396
Deviations from Regression	0.02157	2	0.01074
Error	0.00285	3	0.00095
Total	4.55838	6	

$$F = 11.30 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-6. 3-Picoline 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	10.9532	1	10.9532
Deviations from Regression	0.1069	2	0.0535
Error	0.0291	3	0.0097
Total	11.0892	6	

$$F = 5.45 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-7. 4-Picoline 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.38990	1	0.38990
Deviations from Regression	0.00836	2	0.00418
Error	0.00506	3	0.00168
Total	0.40332	6	

$$F = 2.46 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-8. 2-Ethyl Pyridine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	1.959097	1	1.959097
Deviations from Regression	0.030885	2	0.01544
Error	0.006650	3	0.00222
Total	1.996632	6	

$$F = 6.95 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-9. 2-Benzyl Pyridine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	4.32004	1	4.32004
Deviations from Regression	0.01958	2	0.00979
Error	0.00500	3	0.00166
Total	4.34462	6	

$$F = 5.98 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-10. 4-Benzyl Pyridine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	1.38394	1	1.38394
Deviations from Regression	0.03636	2	0.01818
Error	0.00040	3	0.000133
Total	1.42070	6	

$$F = 136.7 > F_{.05} (2,3)$$

Reject H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-11. 2,4-Lutidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.194915	1	0.194915
Deviations from Regression	0.001304	2	0.000652
Error	0.003100	3	0.001033
Total	0.199319	6	

$$F = 0.63 < F_{.05}(2,3)$$

Accept H: Linearity

Table VI-12. 2,6-Lutidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	8.50500	1	8.50500
Deviations from Regression	0.04009	2	0.02004
Error	0.00256	3	0.000853
Total	8.54059	6	

$$F = 23.49 < F_{.05}(2,3)$$

Accept H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-13. 2,6-Lutidine 1.0 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	1.35494	1	1.35494
Deviations from Regression	0.002670	2	0.001335
Error	0.01420	3	0.00473
Total	1.37181	6	

$$F = 0.282 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-14. 2,6-Lutidine 2.5 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.635168	1	0.635168
Deviations from Regression	0.000046	2	0.000023
Error	0.000844	3	0.000281
Total	0.635258	6	

$$F = 0.078 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-15. 3-Ethyl-4-Methyl Pyridine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	0.340003	1	0.340003
Deviations from Regression	0.019536	3	0.009768
Error	0.004511	3	0.001504
Total	0.364050	6	

$$F = 6.49 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-16. Piperazine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	33.18805	1	33.18805
Deviations from Regression	1.08561	2	0.54285
Error	0.00059	3	0.00020
Total	34.27425	6	

$$F = 2713.25 > F_{.05} (2,3)$$

Reject H: Linearity

TABLE VI -- continued

ANALYSIS OF VARIANCE -- SIX MEMBER COMPOUNDS

Table VI-17. Piperidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	9.46606	1	9.46606
Deviations from Regression	0.02949	2	0.01474
Error	0.00589	3	0.00196
Total	9.50144	6	

$$F = 7.52 < F_{.05} (2,3)$$

Accept H: Linearity

Table VI-18. 2-Methyl Piperidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	13.70904	1	13.70904
Deviations from Regression	0.15920	2	0.07960
Error	0.00796	3	0.00265
Total	13.87620	6	

$$F = 30.04 < F_{.05} (2,3)$$

Accept H: Linearity

TABLE VI ---continued

ANALYSIS OF VARIANCE --- SIX MEMBER COMPOUNDS

Table VI-19. 2,6-Dimethyl Piperidine 0.3 Wt.% N.

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	30.8767	1	30.8767
Deviations from Regression	0.1162	2	0.0581
Error	0.0587	3	0.1935
Total	31.0516	6	

$$F = 2.96 < F_{.05} (2,3)$$

Accept H_0 : Linearity

TABLE VII

REACTION RATE CONSTANTS AT 700°F FOR SIX MEMBER RING COMPOUNDS

Compound	C ₀	K(hr ⁻¹)	95% Confidence Limits
Pyrazine	0.305	13.74	± 1.325
Pyridine	0.342	1.858	± 0.226
Pyridine	0.980	0.576	± 0.0324
Pyridine	2.210	0.214	± 0.0177
2-Picoline	0.301	2.651	± 0.616
3-Picoline	0.319	1.040	± 0.098
4-Picoline	0.306	0.385	± 0.081
2-Ethyl Pyridine	0.301	0.864	± 0.093
4-Ethyl Pyridine	0.296	0.411	± None
4-Isopropyl Pyridine	0.3005	0.125	None
2-Benzyl Pyridine	0.302	2.588	± 0.162
4-Benzyl Pyridine	0.306	--Non-Linear--	
2,4-Lutidine	0.3045	0.272	± 0.063
2,6-Lutidine	0.296	1.800	± 0.058
2,6-Lutidine	1.000	0.718	± 0.135
2,6-Lutidine	2.450	0.492	± 0.033
3,4-Lutidine	0.316	0.0965	None
3,5-Lutidine	0.291	0.279	None
3-Ethyl-4-Methyl Pyridine	0.3655	0.114	± 0.0765
2,4,6-Collidine	0.307	0.512	None
Piperazine	0.307	--Non-Linear--	
Piperidine	0.307	7.944	± 1.01
2-Methyl Piperidine	0.302	9.56	± 2.32
2,6-Dimethyl Piperidine	0.302	6.92	± 0.556
Quinoline	0.288	0.378	None
Acridine	0.2965	0.399	None

TABLE VIII

BOILING POINTS AND REACTION RATE CONSTANTS FOR
MONO-SUBSTITUTED PYRIDINE COMPOUNDS

<u>Compounds</u>	<u>BP (°C)</u>	<u>K (hr⁻¹)</u>
2-Picoline	128.8	2.65
3-Picoline	143.5	1.04
4-Picoline	143.1	0.385
2-Ethyl Pyridine	148.0	0.864
4-Ethyl Pyridine	160.0	0.411*
2-Benzyl Pyridine	276.0	2.588
4-Benzyl Pyridine	286.0	1.465

(* No confidence limits obtained)

TABLE IX

BOILING POINTS AND REACTION RATES CONSTANTS FOR
DI-SUBSTITUTED PYRIDINE COMPOUNDS

<u>Compounds</u>	<u>BP (°C)</u>	<u>K (hr⁻¹)</u>
2,6-Lutidine	142.5	1.80
2,4-Lutidine	158.0	0.272
3,5-Lutidine	Not given	0.279*
3,4-Lutidine	164.0	0.096*

(*No confidence limits obtained)

TABLE X

COMPARISON OF REACTION RATE CONSTANTS FOR
SATURATED AND UNSATURATED NITROGEN COMPOUNDS

Saturated		Unsaturated	
Compound	Reaction Rate Constant	Compound	Reaction Rate Constant
Five Member Ring:			
N-Methyl Pyrrolidine	25.5	N-Methyl Pyrrole	9.93
Six Member Ring:			
Piperidine	7.94	Pyridine	1.86
2-Methyl Piperidine	9.56	2-Picoline	2.65
2,6-Dimethyl Piperidine	6.92	2,6-Lutidine	1.80

TABLE XI

ESTIMATED COEFFICIENTS FOR REGRESSION -- LINEAR MODEL

Compound	B_0	B_1	B_2
Pyrrole	99.814217	-23.692417	-4.6123156
Pyrrolidine	88.418726	-21.878363	-1.8854971
Pyridine	84.404904	-24.445481	-9.7785633
2,6-Lutidine	84.083443	-13.654051	-12.551184

TABLE XII

ANALYSIS OF VARIANCE FOR PYRROLE --- LINEAR MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	8605.5540	2	4302.777
Error	749.6521	15	49.9768
Total	9355.2061	17	

$$F = \frac{ssr}{sse} = \frac{4302.777}{49.9768} = 86.09$$

$$F_{0.01 (2,15)} = 6.36$$

Reject H: $B_1 = B_2 = 0$

TABLE XIII

ANALYSIS OF VARIANCE FOR PYRROLIDINE --- LINEAR MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	8478.4285	2	4239.2142
Error	857.5685	15	57.1712
Total	9335.9970	17	

$$F = \frac{ssr}{sse} = \frac{4239.2142}{57.1712} = 74.15$$

$$F_{0.01 (2,15)} = 6.36$$

Reject H: $B_1 = B_2 = 0$

TABLE XIV

ANALYSIS OF VARIANCE FOR PYRIDINE -- LINEAR MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	9.24.4982	2	4562.2491
Error	1754.2680	15	116.9510
Total	10878.7662	17	

$$F = \frac{ssr}{sse} = \frac{4562.2491}{116.951} = 39.01$$

$$F_{0.01 (2,15)} = 6.36$$

Reject H: $B_1 = B_2 = 0$

TABLE XV

ANALYSIS OF VARIANCE FOR 2,6-LUTIDINE -- LINEAR MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	7105.3877	2	3552.6938
Error	1671.9353	15	111.4623
Total	8777.3230	17	

$$F = \frac{ssr}{sse} = \frac{3552.6938}{111.4623} = 31.87$$

$$F_{0.01} (2,15) = 6.36$$

Reject H: $B_1 = B_2 = 0$

TABLE XVI

COEFFICIENTS OF MULTIPLE CORRELATION --- LINEAR MODELS

<u>Compound</u>	<u>R²</u>
Pyrrole	0.9193
Pyrrolidine	0.9081
Pyridine	0.8387
2,6-Lutidine	0.8095

TABLE XVII

ESTIMATED COEFFICIENTS FOR REGRESSION -- QUADRATIC MODEL

<u>Compound</u>	<u>B₀</u>	<u>B₁</u>	<u>B₂</u>	<u>B₁₁</u>	<u>B₂₂</u>	<u>B₁₂</u>
Pyrrole	103.4699	-42.499924	-1.4676398	5.0149852	0.009507762	-0.00284890
Pyrrolidine	90.623653	-38.537453	-0.23954574	5.2670913	0.00034119008	0.008631528
Pyridine	90.899152	-51.697743	-6.1211845	7.7827277	0.20168093	0.3473014
2,6-Lutidine	93.206561	-33.748778	-9.861724	4.3478323	0.3900971	0.2515156

TABLE XVIII

ANALYSIS OF VARIANCE FOR PYRROLE -- QUADRATIC MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	9169.2483	5	1833.8496
Error	195.9577	12	16.3298
Total	9355.2060	17	

$$F = \frac{(9169.2483 - 8605.5540)}{3(16.3298)} = 11.50$$

$$F_{0.01}(3,12) = 5.95$$

Reject H: $B_{11} = B_{12} = B_{22} = 0$

TABLE XIX

ANALYSIS OF VARIANCE FOR PYRROLIDINE -- QUADRATIC MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	9230.555	5	1846.111
Error	105.442	12	8.7868
Total	9335.997	17	

$$F = \frac{(9230.555 - 8478.4285)}{3(8.7868)} = 28.58$$

$$F_{0.01}(3,12) = 5.95$$

Reject H: $B_{11} = B_{12} = B_{22} = 0$

TABLE XX

ANALYSIS OF VARIANCE FOR PYRIDINE -- QUADRATIC MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	10760.554	5	2154.111
Error	118.212	12	9.851
Total	10878.766	17	

$$F = \frac{(10760.554 - 9124.4982)}{3(9.851)} = 55.41$$

$$F_{0.01 (3,12)} = 5.95$$

Reject H: $B_{11} = B_{12} = B_{22} = 0$

TABLE XXI

ANALYSIS OF VARIANCE FOR 2,6-LUTIDINE -- QUADRATIC MODEL

<u>Source of Variation</u>	<u>S.S.</u>	<u>d.f.</u>	<u>m.s.</u>
Regression	8502.473	5	1700.595
Error	274.850	12	22.904
Total	8777.323	17	

$$F = \frac{(8502.473 - 7105.3877)}{3(22.904)} = 21.60$$

$$F_{0.01 (3,12)} = 5.95$$

Reject H: $B_{11} = B_{12} = B_{22} = 0$

TABLE XXII

COEFFICIENTS OF MULTIPLE CORRELATION -- QUADRATIC MODELS

<u>Compound</u>	<u>R²</u>
Pyrrole	0.9766
Pyrrolidine	0.9887
Pyridine	0.9891
2,6-Lutidine	0.9687

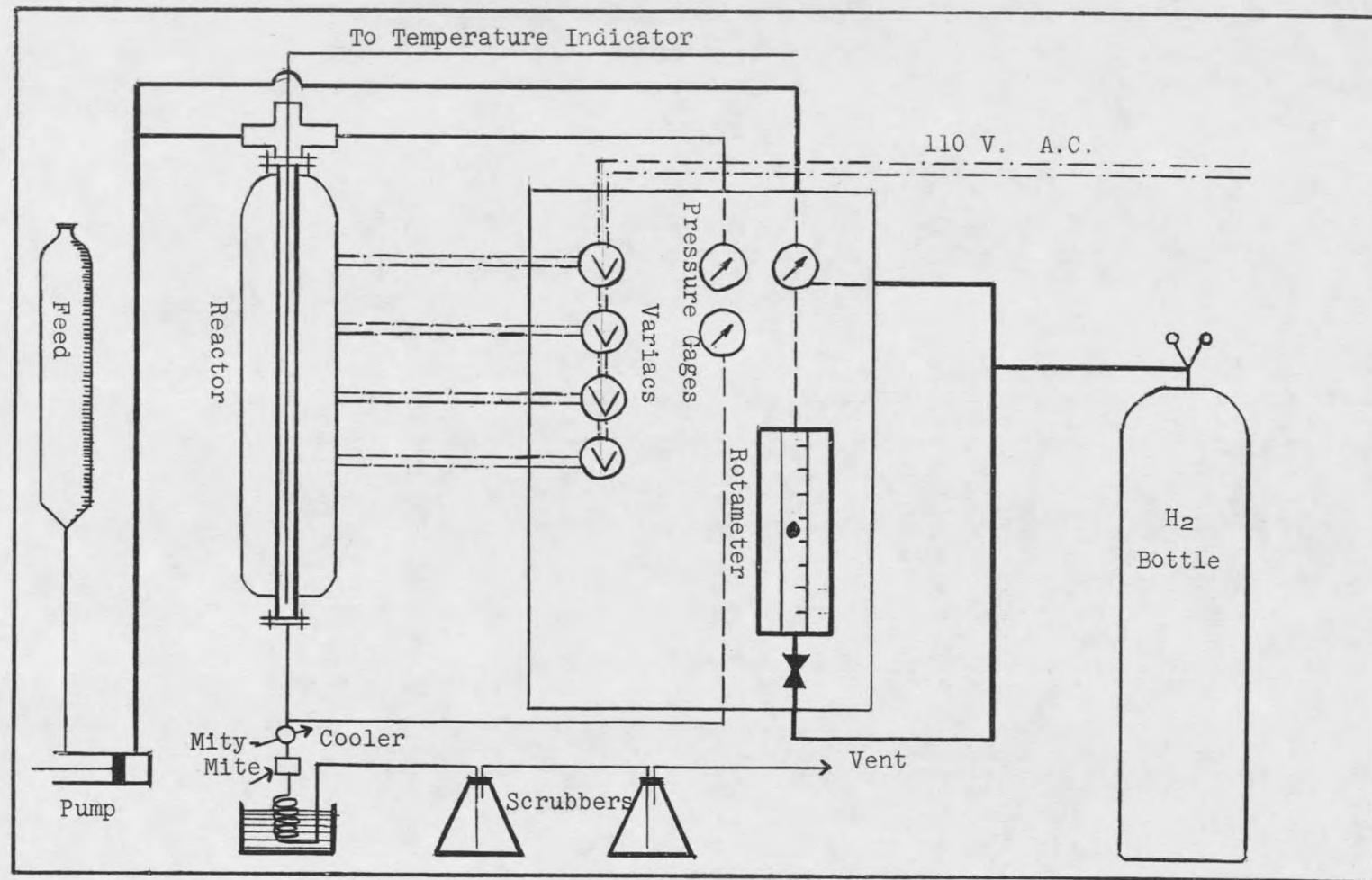


Figure 1. Schematic Flow Diagram

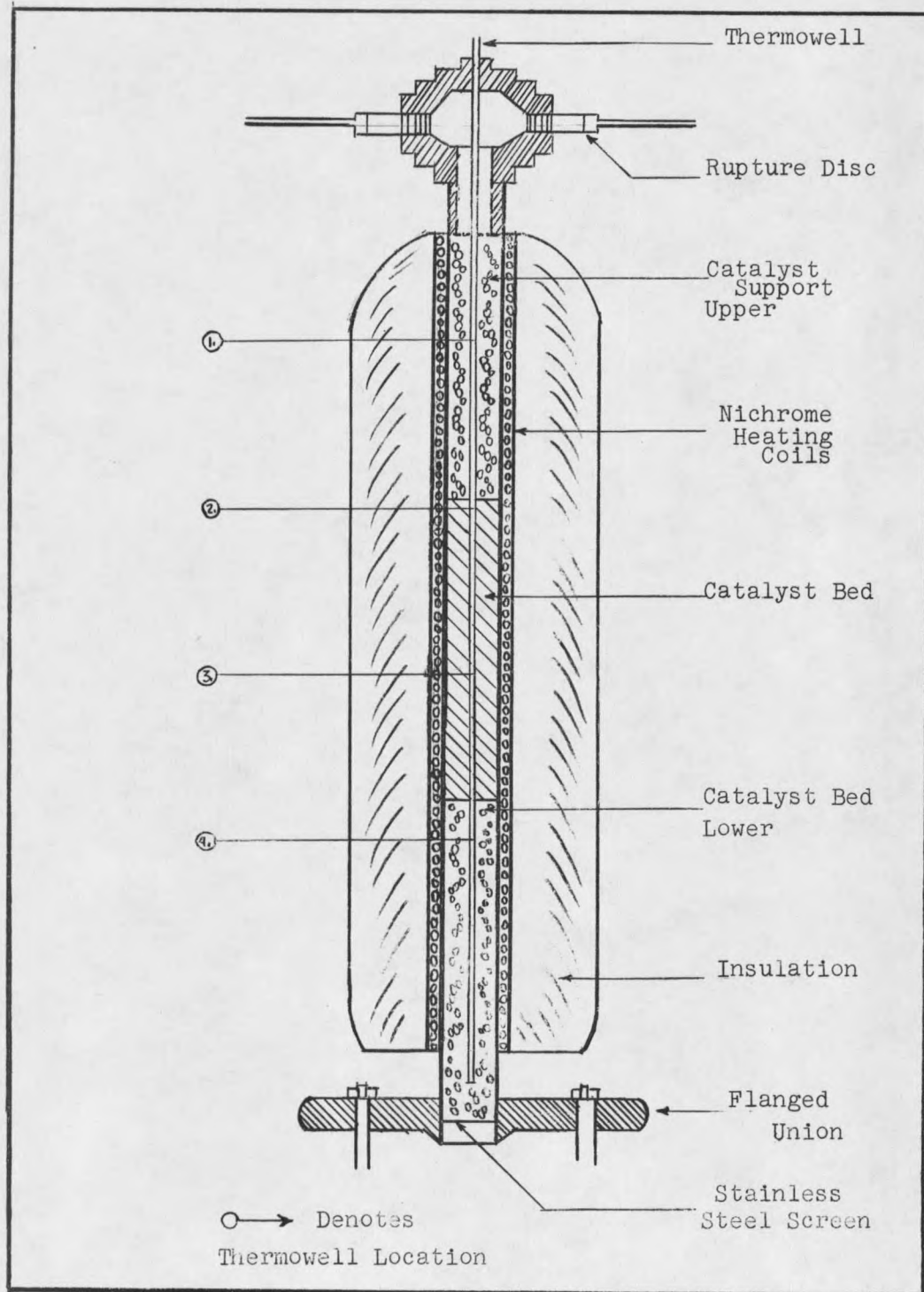


Figure 2. Detailed Diagram of Reactor.

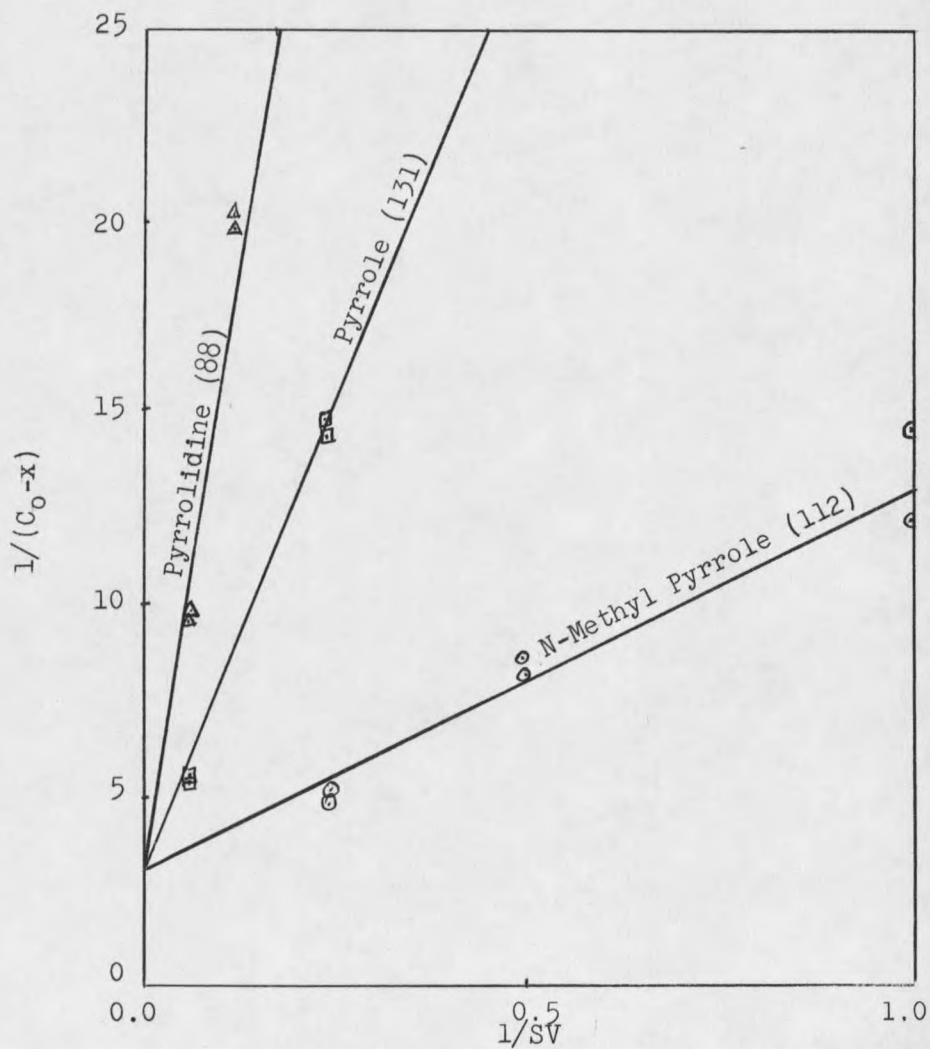


Figure 3. Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity for Five Member Ring Compounds. (Boiling Points °C indicated in parenthesis.)

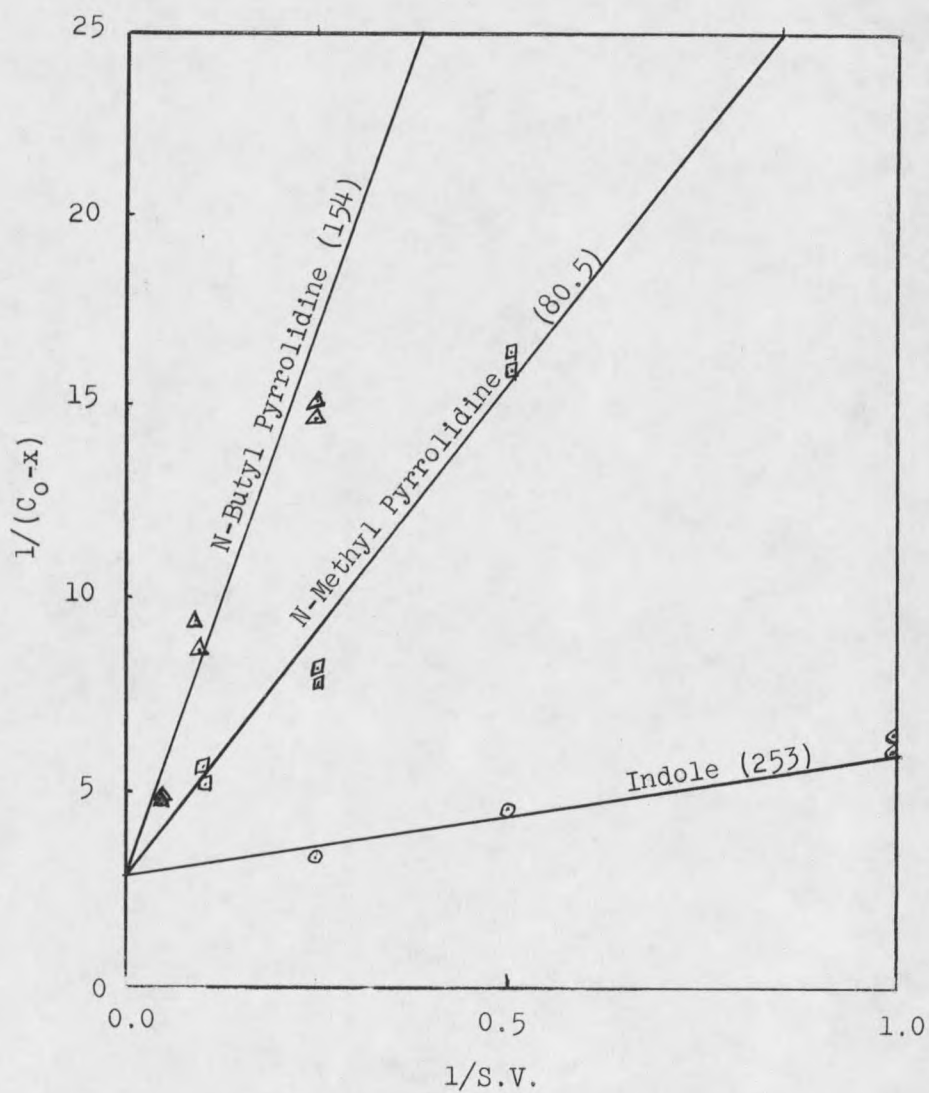


Figure 4. Plot of $1/(C_0 - x)$ vs. Reciprocal Space Velocity for Five Member Ring Compounds.

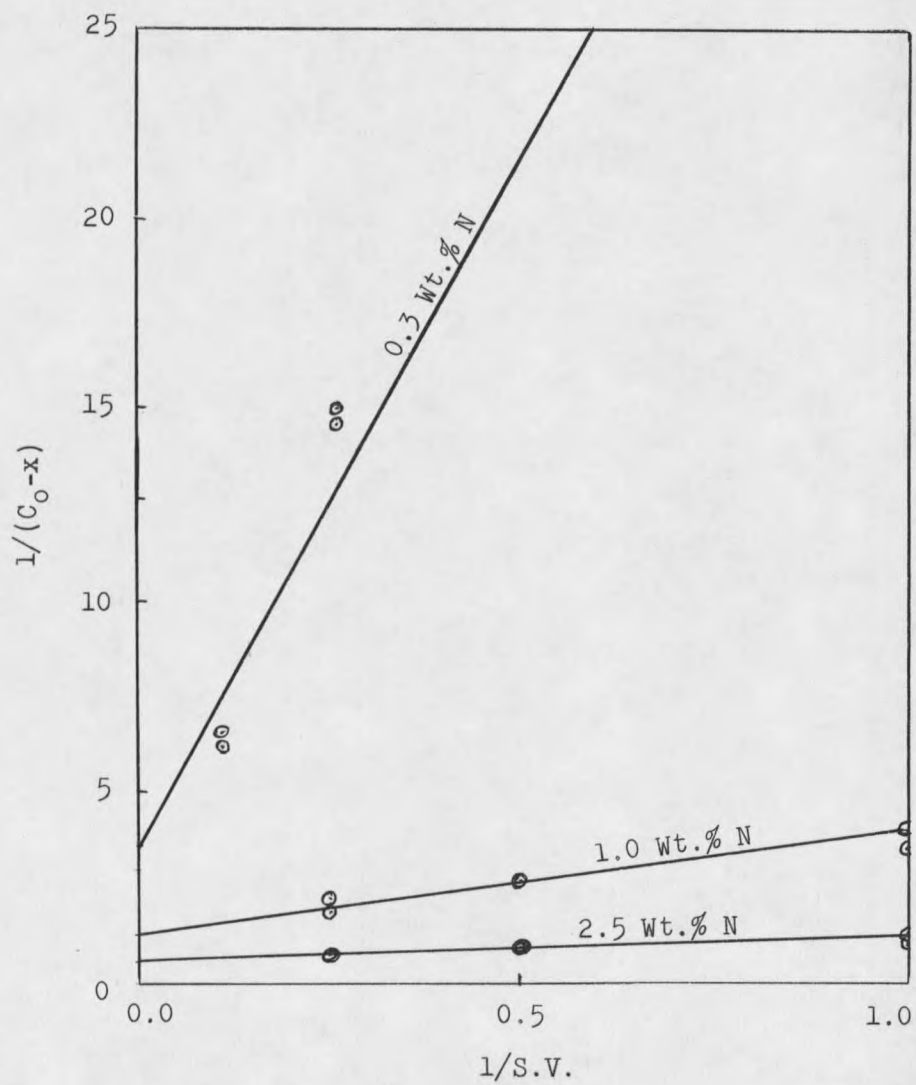


Figure 5. Plot of $1/(C_0 - x)$ vs. Reciprocal Space Velocity for Pyrrole. 0.3, 1.0, 2.5 Wt.% N.

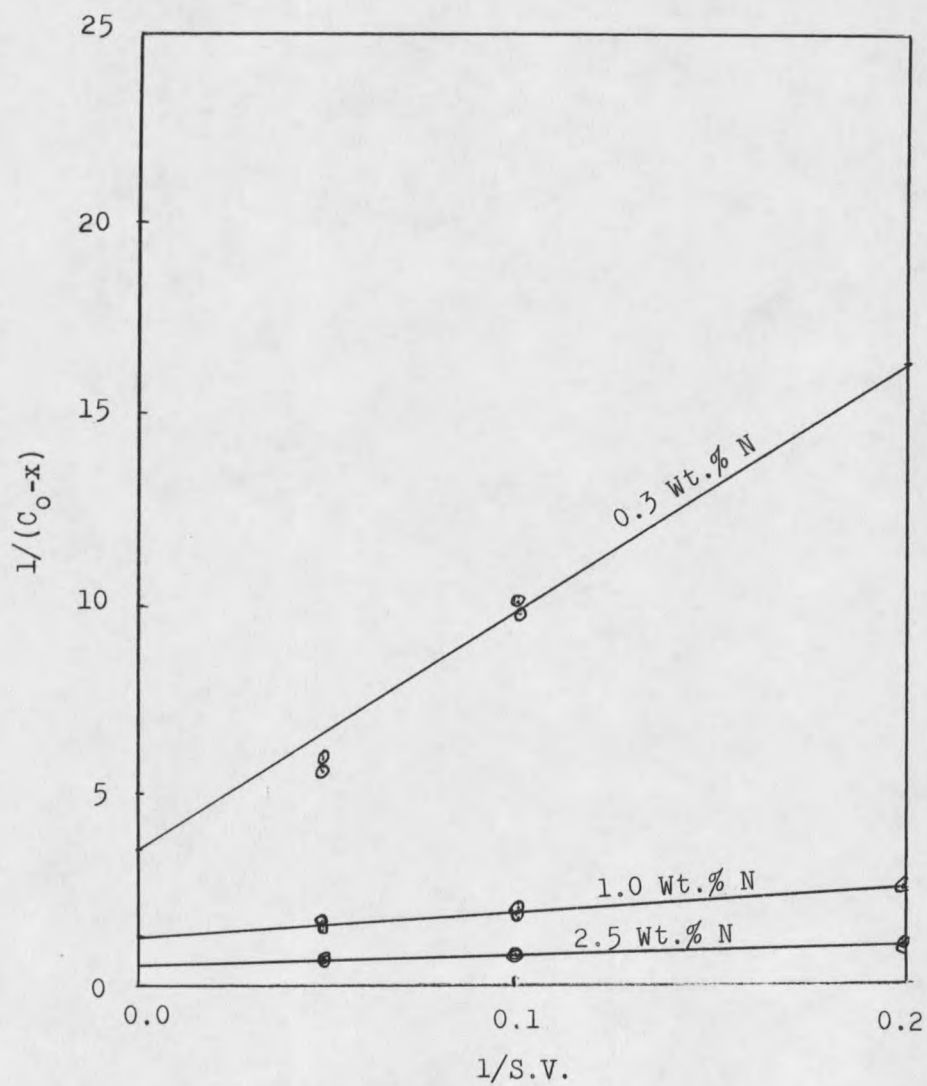


Figure 6. Plot of $1/(C_0-x)$ vs. Reciprocal Space Velocity for Pyrrolidine. 0.3, 1.0, 2.5 Wt.% N.

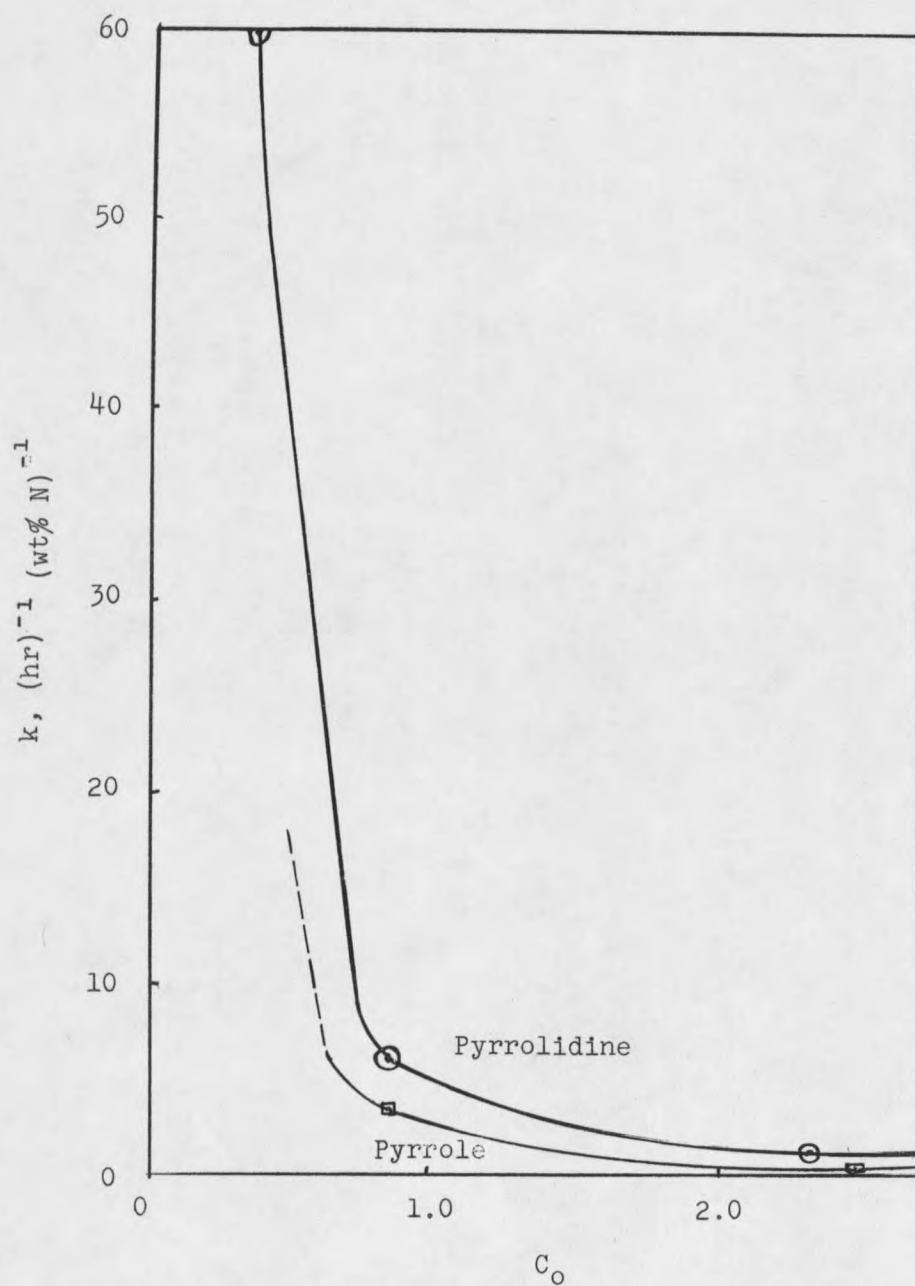


Figure 7. Reaction Rate Constants vs. Initial Nitrogen Concentration for Pyrrole and Pyrrolidine.

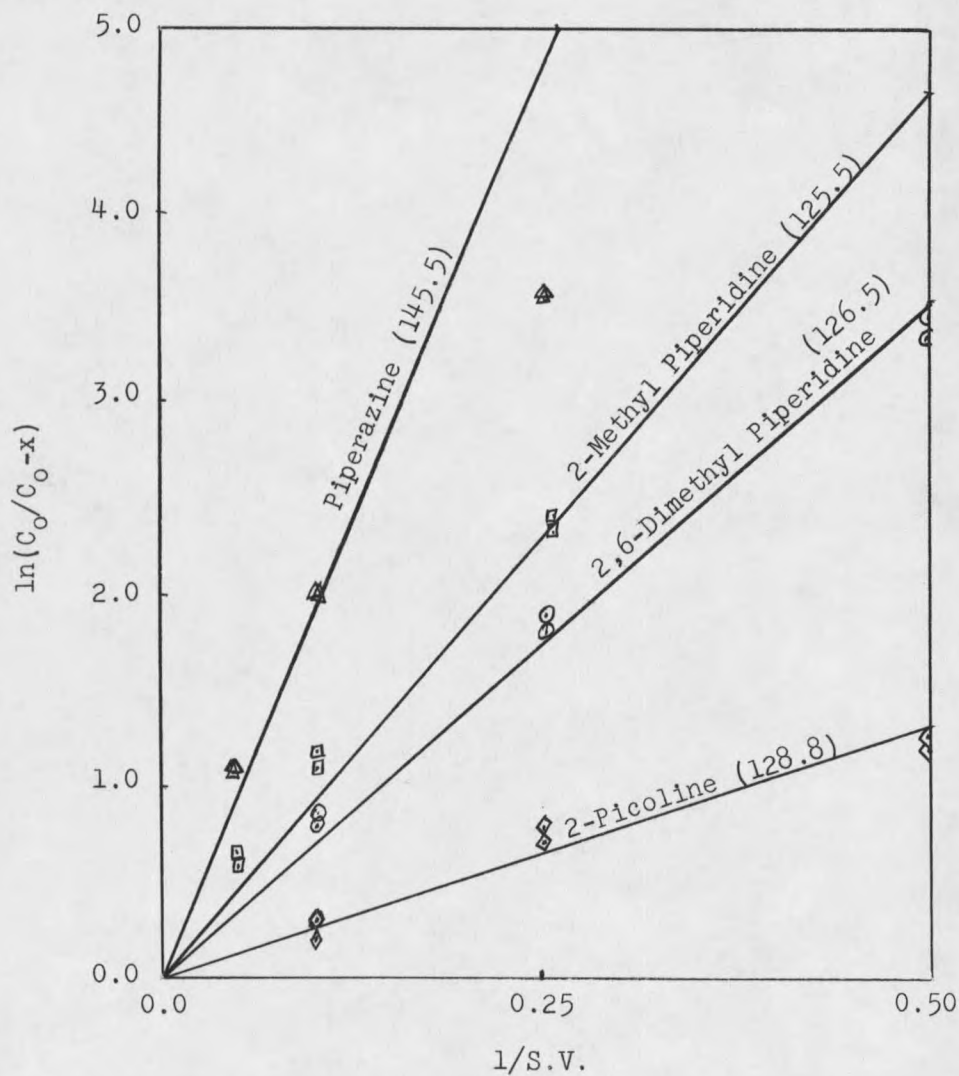


Figure 8. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range 100-140°C. (Boiling Points, °C, in parenthesis.)

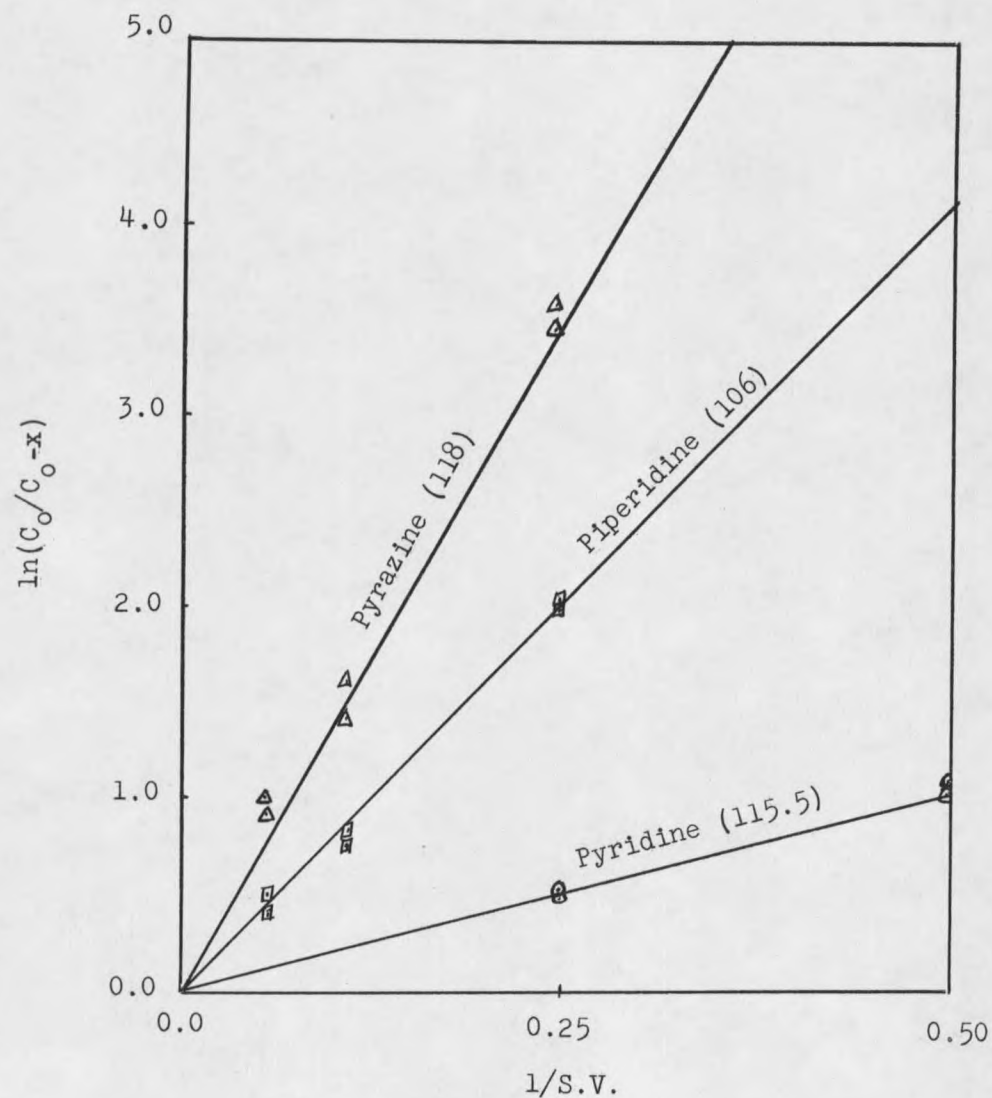


Figure 9. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range 100-140°C. (Boiling Points, °C, in parenthesis.)

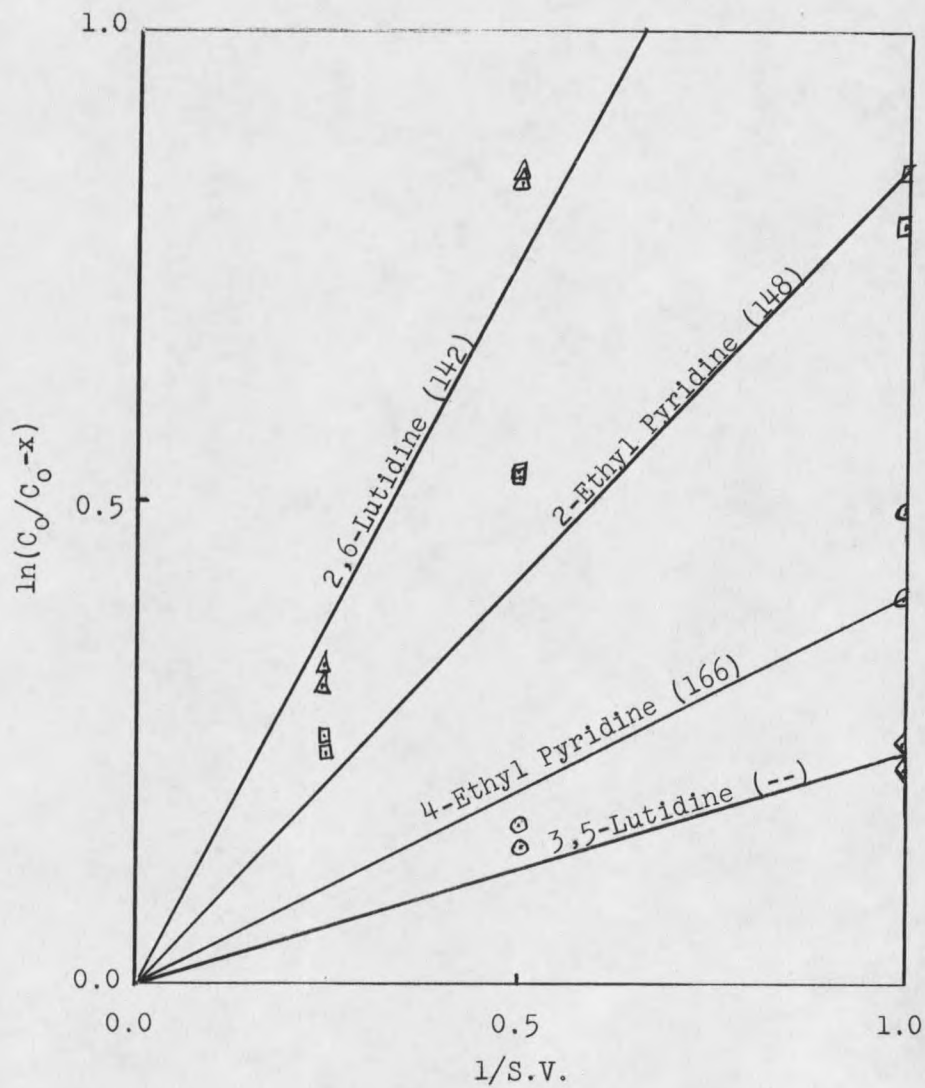


Figure 10. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range 140-170°C. (Boiling Point, °C, in parenthesis.)

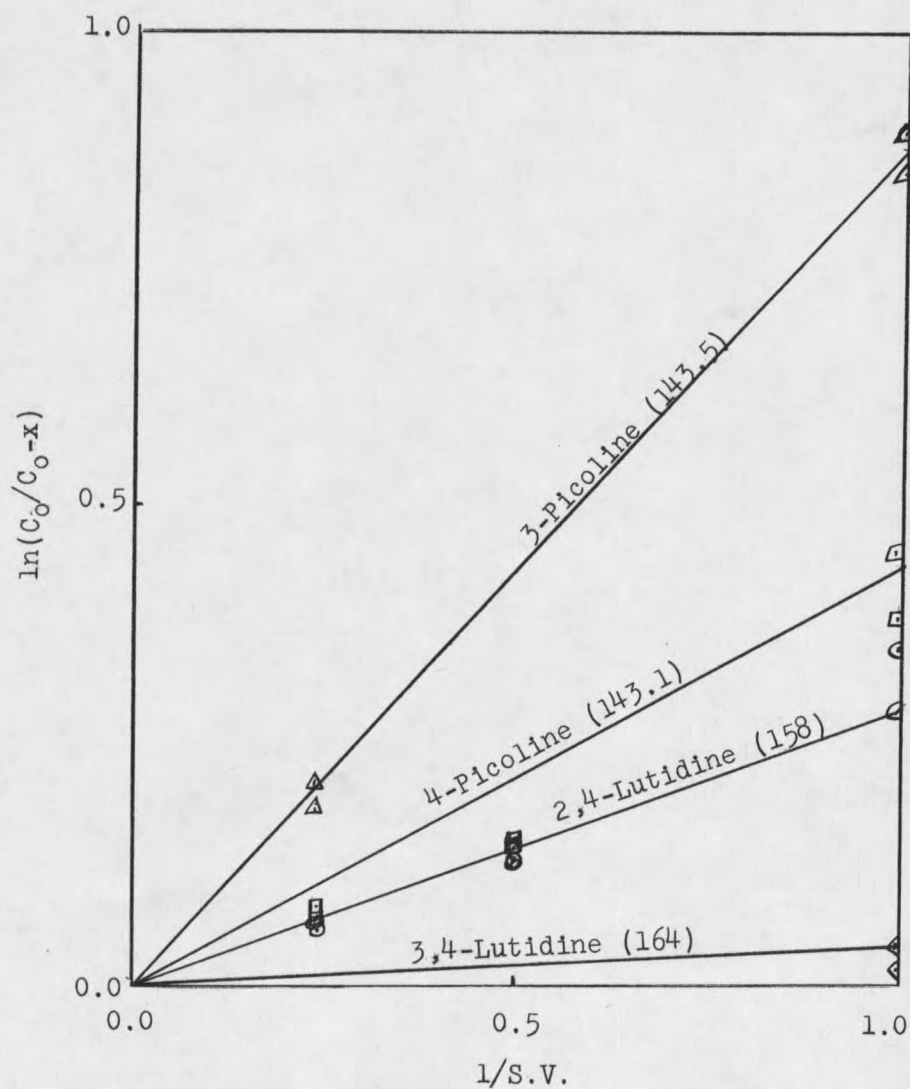


Figure 11. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range, 140-170°C. (Boiling Points, °C, in parenthesis.)

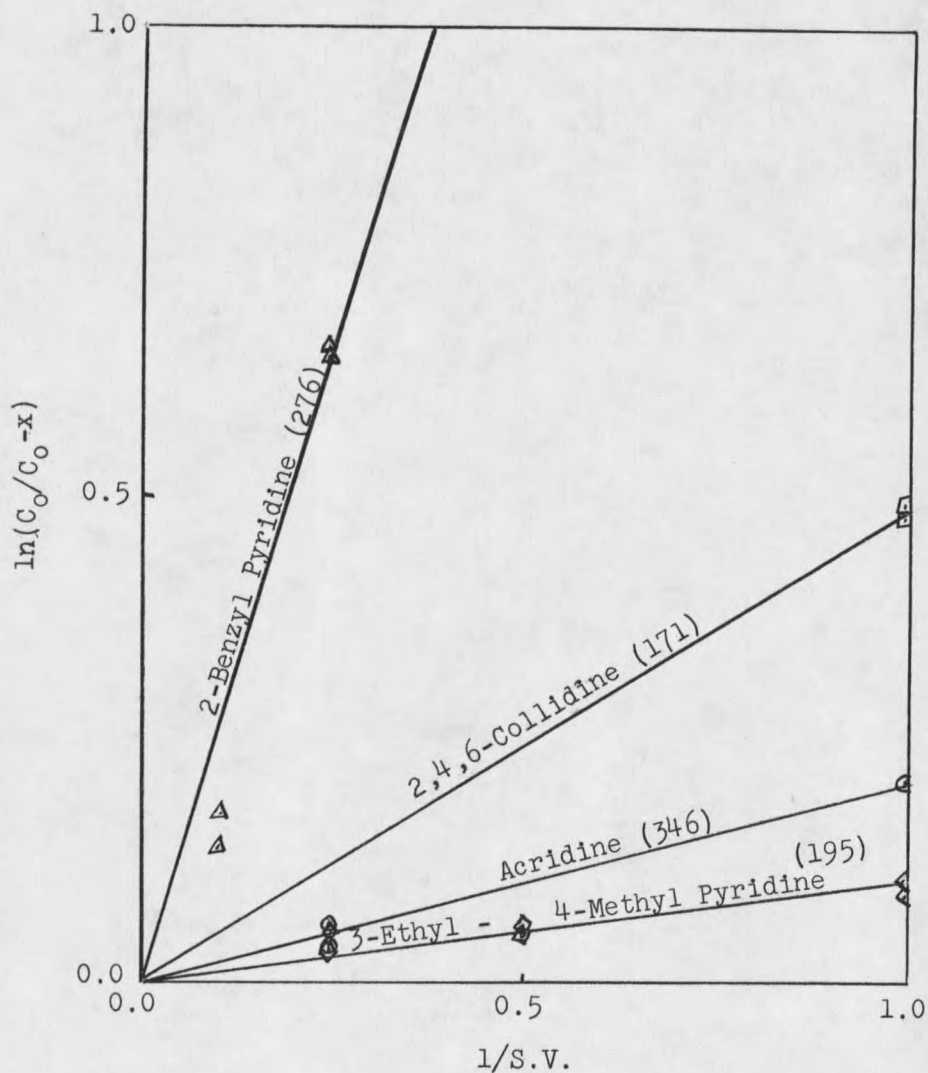


Figure 12. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range 170°-350°C. (Boiling Points, °C, in parenthesis.)

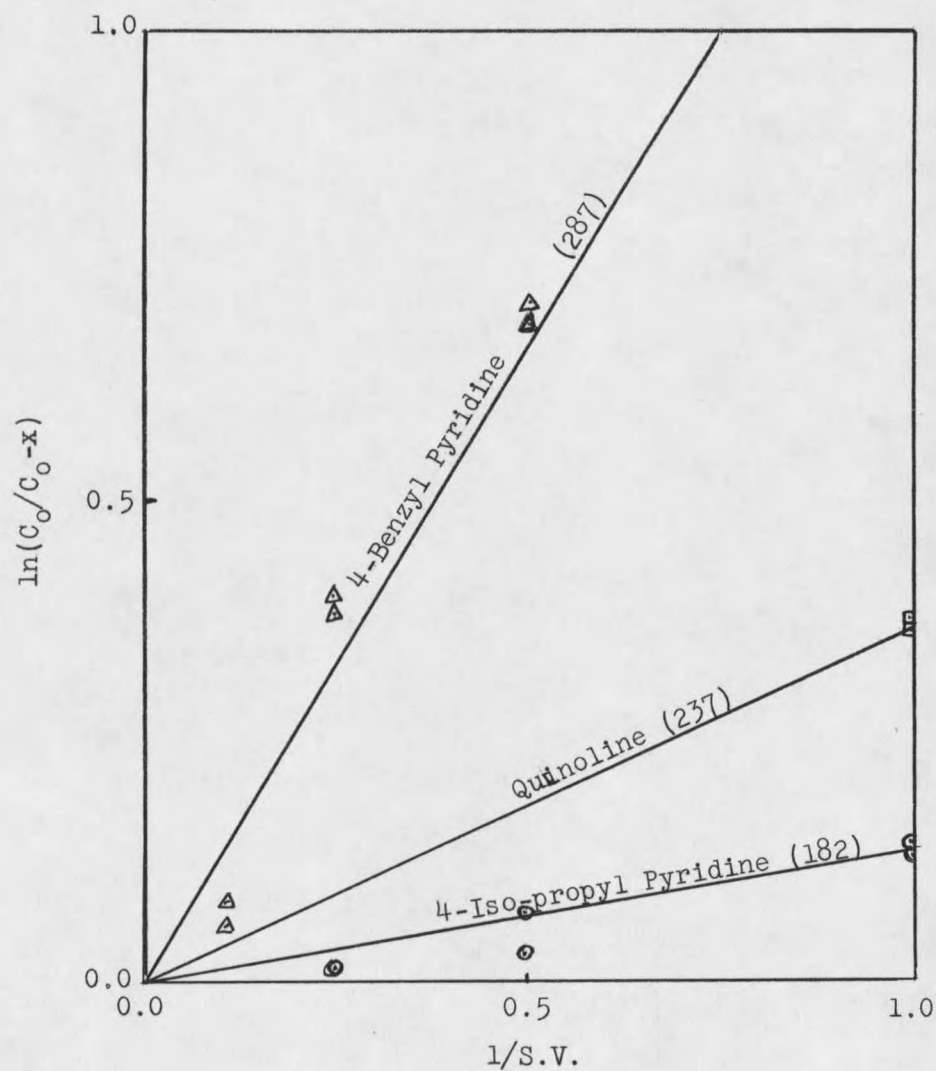


Figure 13. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for Six Member Ring Compounds. Boiling Point Range 170-350°C. (Boiling Points, °C, in parenthesis.)

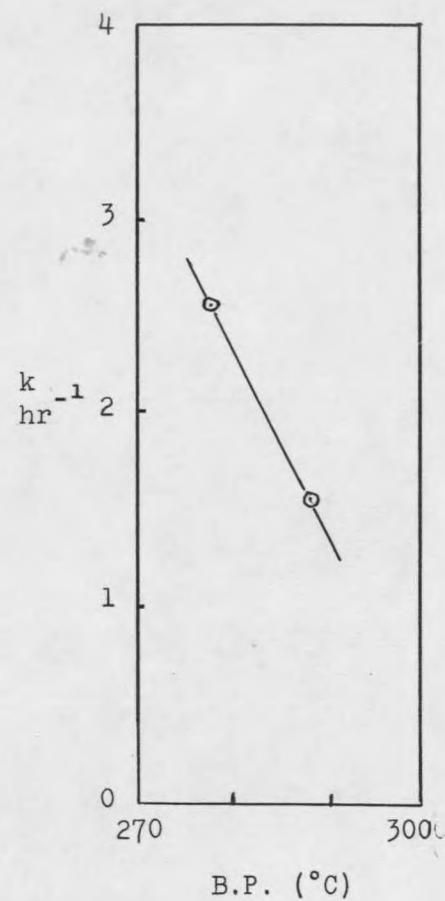
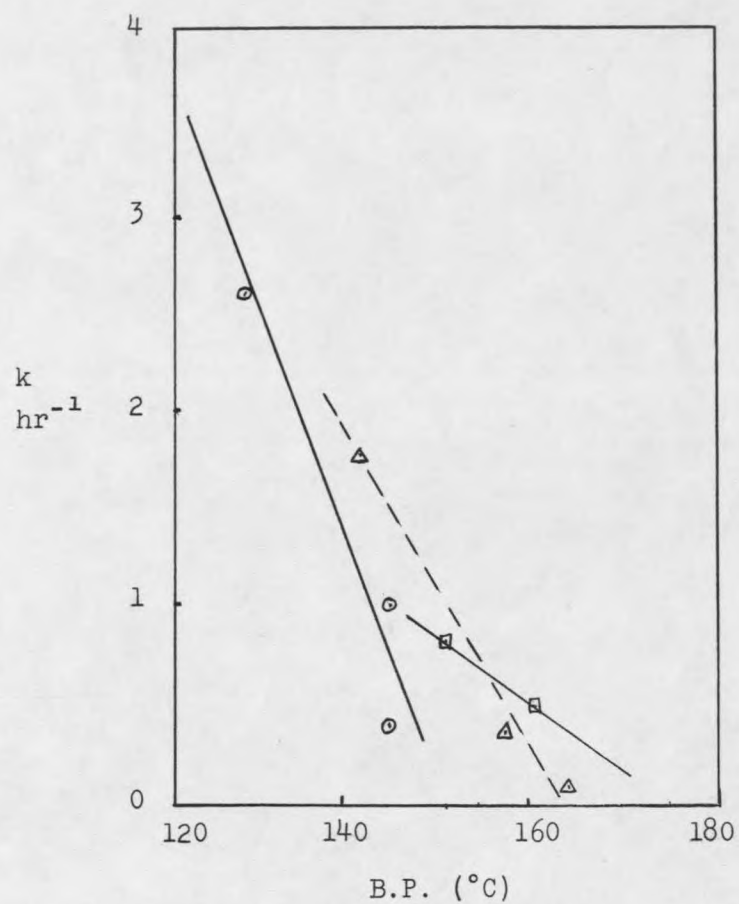


Figure 14. Plot of Boiling Points vs. Reaction Rate Constants for the Mono and Di-Substituted Pyridines.

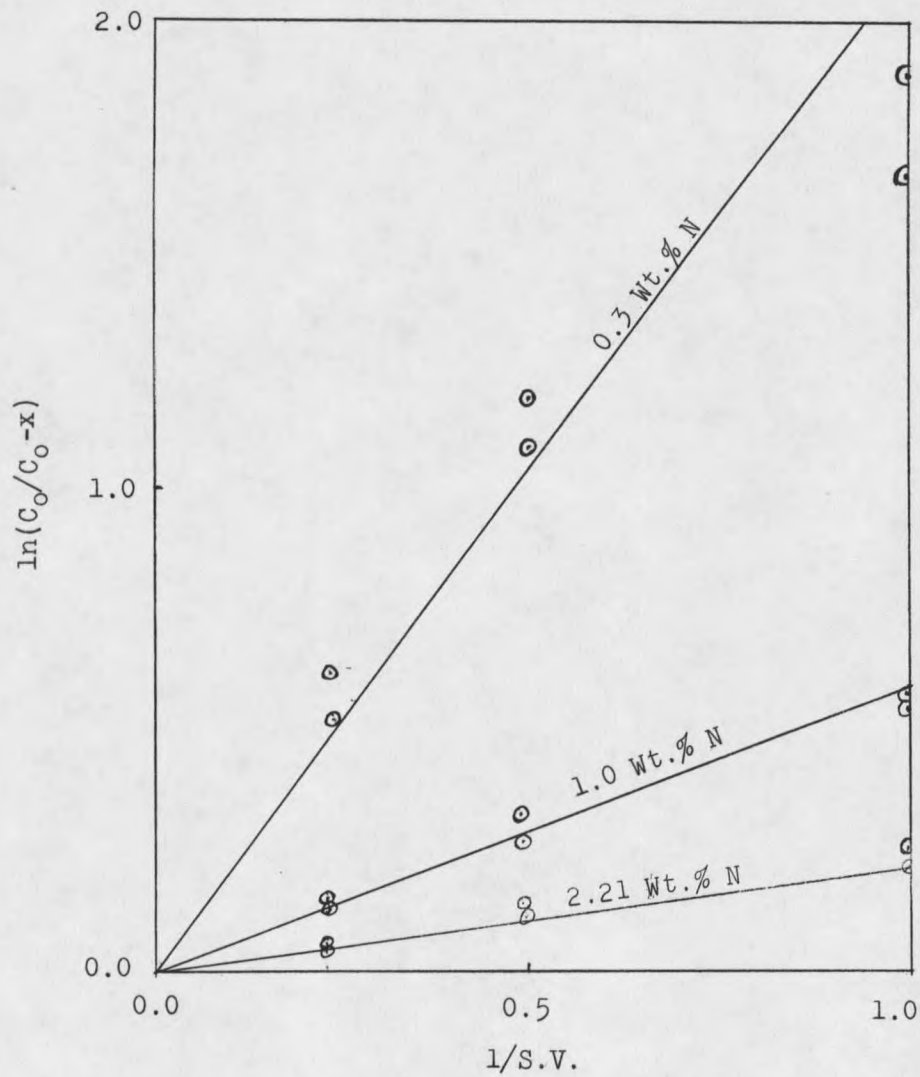


Figure 15. Plot of $\ln(C_0/C_{0-x})$ vs. Reciprocal Space Velocity for Pyridine: 0.3, 1.0, 2.2 Wt.% N.

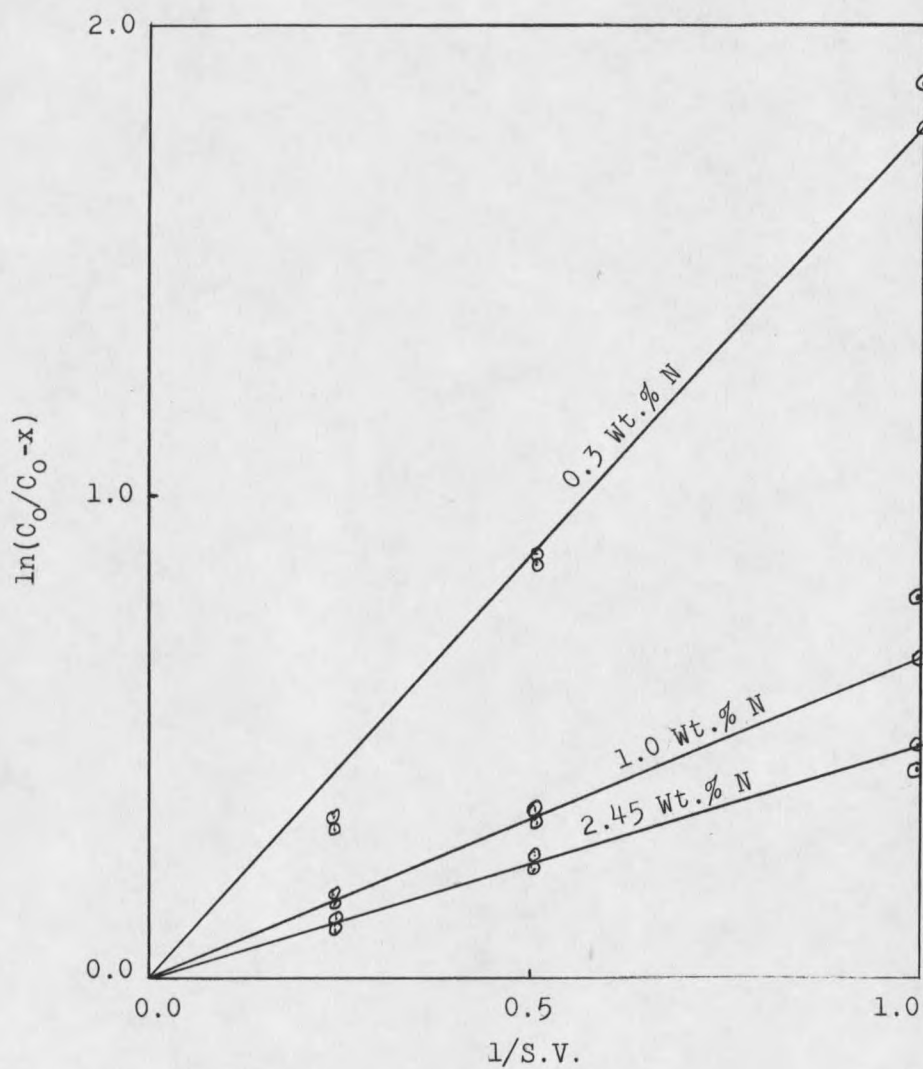


Figure 16. Plot of $\ln(C_0/C_0-x)$ vs. Reciprocal Space Velocity for 2,6-Lutidine: 0.3, 1.0, 2.45 Wt.% N.

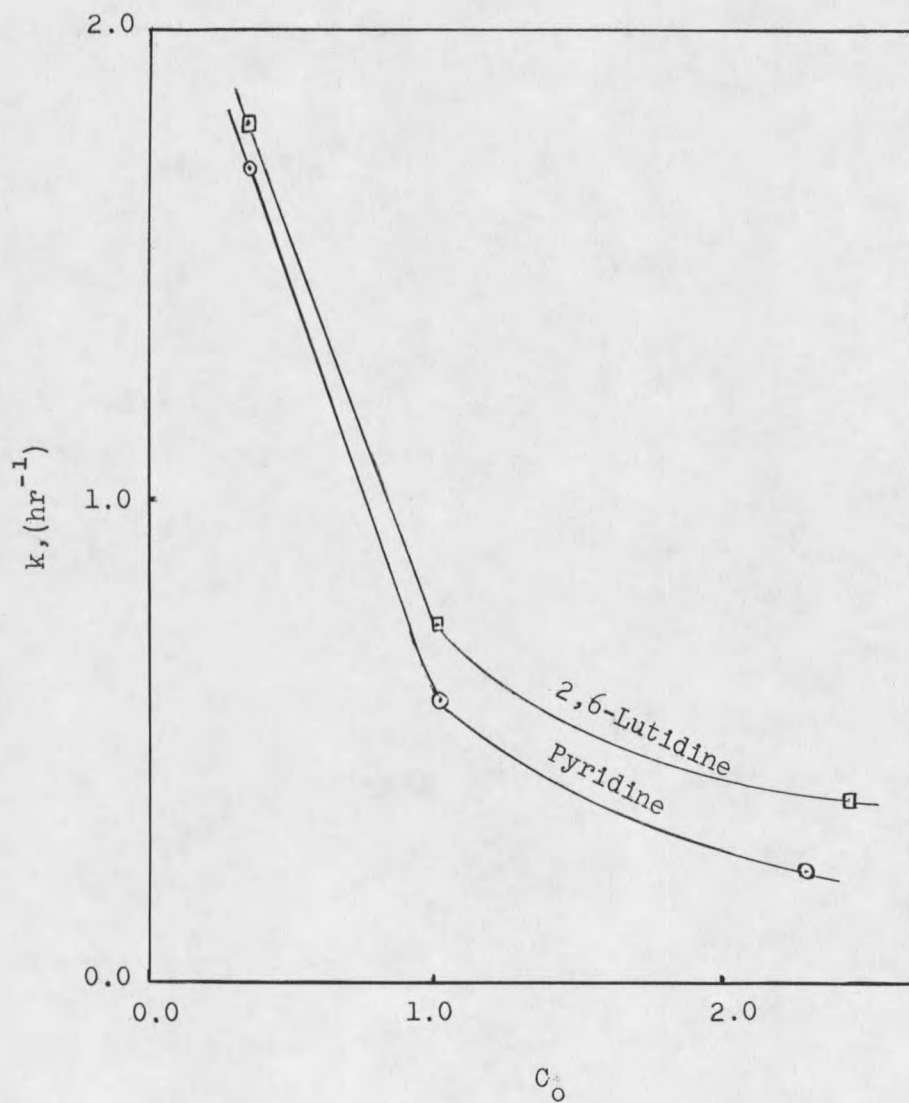


Figure 17. Reaction Rate Constant vs. Initial Nitrogen Concentration for Pyridine and 2,6-Lutidine.

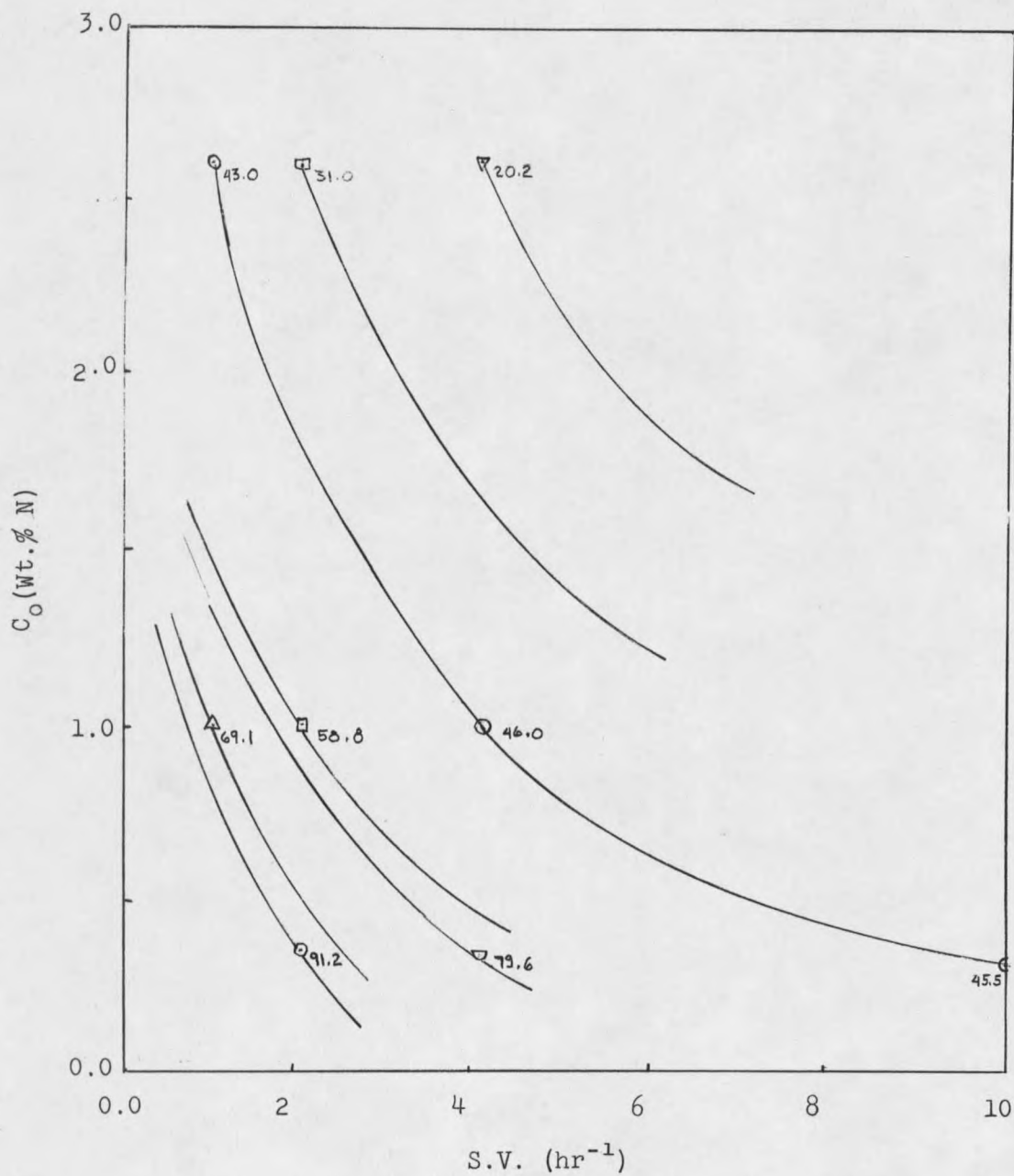


Figure 18. Plot of Percentage Conversion Contour Surface for Pyrrole.

CURRICULUM VITA

Kenneth Edward Cox

PERSONAL

Date and place of birth: May 5, 1936; Tientsin, China

Marital status: Married; no children

EDUCATIONAL

High School: St. Louis College, Tientsin, China; 9/49 to 6/51

Salesian College, London, England; 9/51 to 6/53

Undergraduate: Imperial College of Science and Technology,
University of London, London, England;
9/53 to 6/56. B.Sc. in Chemical Engineering,
A.C.G.I.

Graduate: University of British Columbia, Vancouver, B.C.,
Canada; 9/56 to 6/58. M.A.Sc. in Chemical Engineering.
Montana State College, Bozeman, Montana; 1/60 to 6/62.

EXPERIENCE

Summer Employee with Babcock and Wilcox, Ltd., Boiler Manufacturing plant, Renfrew, Scotland, 6/54 to 8/54.

Summer Employee with Shell Oil of Canada, Montreal Oil Refinery, Montreal, Quebec, Canada, 6/55 to 9/55.

Graduate Assistant in Chemical Engineering, University of British Columbia, 9/56 to 6/58.

Permanent Employee with B. C. Forest Products, Inc., Crofton, British Columbia, Canada, 6/58 to 12/58.

Permanent Employee with Cities Service Research and Development Company, Tar Sands Project, Edmonton, Alberta, Canada, 1/59 to 1/60.

Research Fellow in Chemical Engineering, Montana State College, 1/60 to Date.

CURRICULUM VITA -- continued

EXPERIENCE

Laboratory Teaching Assistant in Chemistry, Montana State College, 9/60 to 3/61.

Tutor to Health and Physical Education Department, Montana State College, 9/60 to Date.

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10009205 3

D378

C838

cop. 3