Rates of destructive hydrogenation of pyrrole and pyridine
by Gary P Schreiber

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

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The destructive catalytic hydrogenation of pyrrole and pyridine has been studied. The purpose of this study was to obtain and evaluate rate data on the destructive hydrogenation of pyrrole and pyridine.

The study was carried out on a bench-scale, continuous-flow,fixed-bed, integral reactor. The range of operating conditions was: temperature 675 to 775°F pressure 250 psig, hydrogen flow rate 7500 SCF/bbl, space velocity 0.50 to 8.0 cc/cc/hr, initial nitrogen concentration 0.2 to 2.0 Wt.% N. The work was done Using an extruded cobalt-molybdate catalyst.

The charge of catalyst varied from 15 to 75 grams.

All calculations here based on the overall nitrogen concentration.

With this basis it was found that the destructive hydrogenation of pyrrole in toluene was a pseudo second order reaction and the destructive hydrogenation of pyridine in toluene a pseudo first order reaction. The energies of activation as calculated from the Arrhenius equation were .10,200 cal/mole for pyridine and 16,890 cal/mole for pyrrole.

It was also noted that a paraffinic diluent resulted in better conversion of pyridine than an aromatic diluent.

Linear and quadratic models were postulated for the regression of the conversion on the process variables, temperature, space velocity, and initial nitrogen concentration. The conversion for the destructive hydrogenation of pyrrole was found to be a linear function of these variables and that for pyridine a quadratic function of the same variables.

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ABSTRACT

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The study was carried out on a bench-scale, continuous-flow, fixed-bed, integral reactor. The range of operating conditions was: temperature 675 to 775°F, pressure 250 psig, hydrogen flow rate 7500 SCF/bbl, space velocity 0.50 to 8.0 cc/cc/hr, initial nitrogen concentration 0.2 to 2.0 Wt.% N. The work was done using an extruded cobalt-molybdate catalyst. The charge of catalyst varied from 15 to 75 grams.

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I INTRODUCTION

The nation's proven reserves of petroleum are increasing yearly and at the same time the petrochemicals industry is expanding rapidly. The petrochemicals industry is putting a large demand on petroleum refiners. Many new syntheses have been developed because of demands for newer and purer chemicals. Are the present sources of chemicals, synthetic and natural, the most economical? This question can be partially answered by research.

In 1944 the United States Congress passed the Synthetic Liquids Fuels Act which authorized research and development on new sources of oil. The main sources of petroleum substitutes appear to be oil-shale and liquid and gaseous products from coal hydrogenation. These sources not only yield many hydrocarbons found in petroleum, but they also yield substantial quantities of organic compounds containing oxygen and nitrogen (1,19).

Much work has been done on the mining and retorting of oil-shale and hydrogenation of coal (8,19-23). One of the big problems now appears to be up-grading the liquids obtained from these processes. Destructive catalytic hydrogenation seems to be a very promising method.

It is desirable to remove completely many of the nitrogen compounds from the above stocks because nitrogen compounds cause catalyst deactivation and gum formation (15). Many nitrogen compounds, however, are in demand in the plastics and resins industries.

For these reasons it would seem desirable to be able to hydrogenate selectively nitrogenous feed stocks. Since the reactions involved are many and complex, much information must be obtained before such a task is undertaken. The catalytic hydrogenation of shale oil fractions has been studied at Montana State College since 1954 (14,17). The majority of the nitrogen compounds found in shale oil and coal hydrogenate are homologs of quinoline, pyridine, and pyrrole. The destructive catalytic hydrogenation of quinoline has been studied at Montana State College by Ryffel (17). To supplement this, it was proposed to study the catalytic hydrogenation of pyrrole and pyridine.

This thesis is a report of such an investigation. The information is of a fundamental nature and should be of value in both the general and selective hydrogenation of feeds containing pyrrole and/or pyridine.

II RESEARCH OBJECTIVES

The objectives of this research were to gather and evaluate data from the destructive hydrogenation of pyrrole and pyridine. The main objective was to obtain kinetic data on the decomposition of these two compounds. We were interested in determining the following:

1. The empirical order of reaction
2. The effect of changing the following process variables:
   a. temperature
   b. space velocity
   c. initial concentration of nitrogen
   d. type of carrier or diluent
3. An equation relating the conversion to temperature, space velocity, and initial concentration of nitrogen in a fixed diluent

The above objectives were realized insofar as time and available equipment allowed. The research was meant to be of a fundamental nature but designed so that the results could be applied to the broader problem of destructive hydrogenation of feeds containing pyrrole and pyridine.

III EXPERIMENTAL CONSIDERATIONS

A. Introduction

Selection of Feedstock: In order to simulate commercial feedstocks, it was necessary to find hydrocarbon carriers and nitrogen compounds characteristic of those found in commercial stocks, but still avoid complex mixtures. The compounds to be used had to be reasonably priced and available in 5-gallon lots.

The literature (1,2,19) reports that the nitrogen in commercial stocks is present primarily as homologs of pyridine, pyrrole, and quinoline. Since an extensive study on quinoline had been carried out by Ryffel (17) at Montana State College, it was decided to use pyrrole and pyridine as the nitrogen compounds in this study.

Commercial feedstocks contain many hydrocarbons, most of which may be classed as either aromatic, naphthenic, or paraffinic. For this reason it was decided to use a carrier from each of the above classes. Those carriers chosen were toluene, methylcyclohexane, and normal heptane. In order to check the experimental results, cumene (iso-propylbenzene) was used in several runs. Some physical properties (9) of the carriers used are:

Compound	M. Wt.	B. P., °C	Density, g/ml
Toluene	92.13	110.63	0.8669
Methylcyclohexane	98.18	100.3	0.7864
normal Heptane	100.2	98.43	0.6838
Cumene	120.19	152.40	0.8618

Process Conditions: The process conditions for this study were chosen after several exploratory runs were made and from previous knowledge of hydrogenation processes. Consideration was given mainly to keeping the conversion in the 10-90 per cent range. The limitations of the equipment and analytical techniques and the time requirement were also considered. The process conditions finally chosen were as follows:

Pressure: constant at 250 psig
Temperature: 675 to 775°F
Hydrogen Flow Rate: 7500 SCF/bbl feed
Initial Nitrogen Concentration: 0.20 to 2.0 Wt.% N
Space Velocity: 0.50 to 8.0 cc/cc per hour
Catalyst: CoMo, 15 to 75 grams

Thermodynamic Study: A thermodynamic study of the hydrogenation of pyrrole and pyridine is given in the Appendix. This study was done to verify the thermodynamic feasibility of the over-all reactions of pyridine plus hydrogen, and pyrrole plus hydrogen to yield ammonia and various hydrocarbons. For example, the free energy changes and equilibrium constants at several temperatures are:

Temp., °K	$\Delta F°$, cal/mole		K_{eq}	
	Pyridine	Pyrrole	Pyridine	Pyrrole
300	-45,120	-60,420	5.02×10^{32}	5.5×10^{43}
500	-23,160	-52.620	1.2×10^{16}	7.5×10^{22}
700	+ 80	-44,890	1.06	8.3×10^{13}

The temperature of neutral equilibrium for pyridine was calculated to be 690°K while that for pyrrole was 1,860°K. Thus, the reactions appeared favorable at the temperature range investigated. The complete study with the results at four temperatures and four pressures is included in the

Appendix.

B. Materials

Feedstock: The diluents used (toluene, methylcyclohexane, n-heptane, and cumene) were all technical grade and were purchased in 5-gallon lots from Phillips Petroleum Company. The pyridine and pyrrole were commercial grade reagents. The pyridine was purchased from Eastman Organic Chemicals, the pyrrole from Ansul Chemical Company.

The feed stock was prepared by mixing the appropriate amount of pyrrole or pyridine with the desired diluent. Since the initial concentration of nitrogen was a variable in these studies, only about one gallon of feed was prepared at one time.

Catalyst and Catalyst Supports: Previous hydrodesulfurization and hydrodenitrogenation studies conducted at Montana State College in conjunction with Esso Research and Engineering Company (6,13), the Engineering Experiment Station (14), and the National Science Foundation (17) have shown that a cobalt-molybdenum catalyst is effective in hydrogenation processes. The catalyst used here consisted of a mixture of cobalt and molybdenum oxides on an alumina carrier. In particular, it was Nalco-Esso cobalt-molybdenum 1/16-inch extruded catalyst.

The catalyst bed was supported on top and bottom in the reactor by 1/8-in. and 1/4-in. low surface area alumina pellets. When dilution of the catalyst was necessary, the 1/8-in. alundum pellets were used. The catalyst plus pellets occupied a volume of about 100 cc in the reactor.

Hydrogen Treat Gas: The hydrogen treat gas was purchased in high pressure cylinders from HR Oxygen and Supply, Billings, Montana. The hydrogen was first passed through a "Deoxo" unit where trace oxygen is converted to water. The water was removed by passing the hydrogen-water mixture through a drying unit containing "Drierite" and an indicator. The purpose of the indicator was to show when the "Drierite" was spent.

C. Equipment

Flow Diagram: A schematic flow diagram of the experimental unit is shown in Fig. 1. The reactor is operated as a fixed-bed, continuous-flow integral reactor. Feed stock is pumped from the reservoir into the top of the reactor where it is joined by deoxygenated and dried hydrogen. The feed and hydrogen then pass down through the pre-heat, catalyst, and after-heat zones together. The vapors are condensed while still under pressure. After passing through the pressure regulator, the gaseous and liquid products are passed through a cooling coil in an ice bath. The liquid product is collected in a flask, while the gases are acid scrubbed and vented to the atmosphere.

Specifications: The reactor was made from 1-in. OD, seamless, schedule 80, stainless steel pipe 30 inches in length. The bottom of the reactor was silver soldered to a flanged union to permit ease in assembling and charging. The top of the reactor was permanently connected to a high pressure cross with a 1500 psi rupture disc inserted as a safety precaution. The reactor was covered with a layer of asbestos tape and then wrapped with five ceramic-beaded nichrome heating coils.

A 1-1/2 in. layer of 85% magnesia insulation was placed over the heating coils.

A thermowell was passed down through the center of the reactor slightly past the flanged union. This allowed ease of centering the thermowell while charging the reactor. A 3/16-in. OD stainless steel tube, sealed at the lower end, was used for the thermowell. Five iron-constantan thermocouples were placed inside the well for measuring the temperature at various positions throughout the reactor. The diagram indicating the positions of the thermocouples, heating coils, and catalyst zone is shown in Figure 2.

Additional equipment also used was as follows: a Lapp Pulsafeeder pump; a Brooks armored high pressure rotameter with a 3/32-in. ball; a Grove (Mity-mite) back pressure regulator; five 110-volt Powerstats; a 1000 ml glass feed reservoir with a 50 ml graduated burette attached for measuring volumetric flow; a Leeds and Northrup indicating potentiometer; four Marshalltown 2000 psi test gauges; a Dohor Deoxo Purifier; a Matheson hydrogen regulator.

All tubing used on the unit was type 302 stainless steel, 1/8-in. OD tubing. Various Hoke valves were also used on the unit.

D. Operating Procedures

Feed Stock Preparation: Feed stock was prepared just prior to running; the amount prepared depending upon the immediate need. The method of preparation was simply to add the required amount of pyrrole or pyridine to a given weight of diluent.

Reactor Preparation: Before each run the reactor, condenser, and Mity-mite pressure controller were cleaned with acetone. After cleaning, the reactor was charged by inverting the reactor, pouring in catalyst supports to a desired level, adding catalyst (diluted to 100 cc with catalyst supports when necessary), and filling the remainder of the tube with catalyst supports. The reactor was tapped lightly at intervals during the charge to insure good settling of the filler. The charge was held in the reactor by inserting a stainless steel screen into the bottom of the reactor. The reactor was then placed in the proper position and connected with the rest of the system. The unit was then purged with hydrogen at atmospheric pressure to remove the air. It was then pressurized and tested for leaks. If no leaks were found, it was ready for a run.

Operation: In preparing for a run, the reactor was pressurized and heated overnight in a hydrogen atmosphere. The feed pump was started when the unit was about 20° below the desired operating temperature. The temperature was then brought up rapidly to operating conditions. The feed rate was controlled by adjusting the pump to give the desired volumetric feed rate. The hydrogen was metered through a rotameter and the flow adjusted with a needle valve. The temperature was recorded every half hour and the Powerstats adjusted when necessary. The pressure was controlled by a Mity-mite regulator which occasionally needed adjusting. The processed oil was collected in a receiver below the Mity-mite after passing through an ice-bath. The purpose of the ice-

bath was to minimize loss of volatile products.

Sampling: The unit was allowed to run from three to ten hours after operating conditions were reached (line-out) before a sample was taken. This was done to allow the catalyst to "settle down". The time-period after line-out depended upon the severity of the operating conditions. Low space velocity and high temperature are considered severe. Three samples were then taken, the length of sampling time depending upon the feed rate, at one- to two-hour intervals. Each sample was analyzed and the conversions compared to ensure complete line-out.

E. Analytical Procedures

The weight per cent nitrogen in the samples and feed stock was determined by the standard Kjeldahl method (11). Two determinations were run on each sample and the results averaged. The conversion was then calculated using these and the feed stock concentrations.

Some of the samples were then analyzed with a vapor-phase chromatograph to give a rough idea of the products. The samples from the pyrrole runs contained compounds which did not resolve on the chromatograph. One of these was then analyzed with a recording infrared spectrophotometer. The chromatographic analysis of the products from hydrogenated pyridine indicated that the nitrogen present was almost exclusively pyridine. The infrared analysis of the product from hydrogenated pyrrole indicated the presence of a complex mixture of primary and secondary amines.

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 (7,18). If we base the rate of reaction on a reactant having a concentration C at any time t, we may express the rate of reaction r as

$$r = \frac{-dC}{dt}$$

The law of mass action states that the reaction rate r of a chemical reaction is proportional to the products of the "active masses" of the reactants involved. The actual activity of a substance in a mixture is often difficult to obtain. For this reason concentrations are usually used in place of active masses. Thus, if we have two reactants A and B reacting to give products R and S, for example

$$A + B \longrightarrow R + S$$

the rate may be expressed as

$$r = \frac{-dC_A}{dt} = kC_A^a C_B^b$$

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

The constant k in the above reaction is called the reaction rate constant. In general, the rate constant is constant only at fixed temperature and pressure. The units of k depend upon the concentration units involved and the order of reaction. The order of the above reaction is defined to be a plus b. The order of a reaction may have values from 0 to 3 including fractions.

The rate equation above is derived for homogeneous systems but has been found suitable for many heterogeneous systems also. This is particularly true when one or more of the reactants is present in large excess. In most hydrogenation reactions, for instance, the hydrogen is present in such an excess that the change in concentration of hydrogen is negligible.

For a heterogeneous reaction such as

Pyridine + Hydrogen $\longrightarrow$ Hydrocarbons & Ammonia

the rate may be expressed as

$$r = \frac{-dC_P}{dt} = kzC_P^p C_H^h$$

where k is the rate constant, C_P and C_H are the concentrations of pyridine and hydrogen respectively, and z is a catalyst factor. When the hydrogen is in excess, the rate constant k, the catalyst factor z, and C_H may be incorporated into a new constant k' so that the rate equation becomes

$$r = \frac{-dC_P}{dt} = k' C_P^p$$

For purposes of data analysis, the above equation is more convenient in the form

$$\frac{-dC_P}{dt} = k'(C_{P_o} - x)^p$$

where C_{P_o} is the initial pyridine concentration and x is the amount of pyridine converted. Since the analytical methods used in this study were for nitrogen, not pyridine, the equation should be written

$$r = \frac{-dC_N}{dt} = k'(C_{N_o} - x)^n$$

where the N denotes nitrogen. It is also convenient when dealing with

only one reactant other than hydrogen to drop the subscript N. Thus the equation used would be

$$\frac{-dC}{dt} = k'(C_o-x)^n$$

where C denotes the concentration of nitrogen whether dealing with pyridine or pyrrole. One should note that

$$C = C_o-x$$

$$dC = -dx$$

Thus replacing dC by -dx, separating variables, and integrating from x = o to x = x and t = o to t = t we have

$$\int_o^x \frac{dx}{(C_o-x)^n} = \int_o^t k'dt = k't$$

where the integral on the left depends upon n. The term t represented here is the actual contact time with the catalyst. Since this actual contact time is difficult to obtain, it is convenient to replace it by a term proportional to it. This term is the space velocity, SV. The space velocity is defined as the volume or weight of reacting mass per volume or weight of catalyst per unit time. The volume of catalyst is not standard, e.g. it is often taken as volume occupied by catalyst before packing in a reactor or by volume of reactor occupied by catalyst. In this study the space velocity was taken as volume of oil per volume of catalyst before packing per hour. It is seen from this basis that reciprocal space velocity has the units, hours.

With the above modification the integral rate equation becomes

$$\int_{0}^{x} \frac{dx}{(C_o-x)^n} = K/SV$$

where K is the new constant incorporating the proportionality factor between t and 1/SV.

B. Order of Reaction

The order of the above reaction is then n where n is the exponent on the (C_o-x) term. It should be noted that under the modifications made and the fact that hydrogen is in excess, the order here is said to be "pseudo order".

The common method for determining n is to assume different orders of reaction until one is found which correlates with the data. Some common orders tried are 0, 1/2, 1, 3/2, and 2. It sometimes happens that one or more choices of n appear to correlate with the data. In such a case it is accepted to take the simplest mathematical expression. For example, if n = 1/2 and n = 1 both appear to yield straight lines when applied to the data, it is convenient to use the first (n = 1) order expression. It is not too uncommon to encounter data which satisfies no common order, in which case it may be necessary to use other methods of analysis such as multiple regression.

C. Energy of Activation

The reaction rate constant is generally constant only at constant temperature and pressure. The effect of temperature on the reaction rate constant is usually expressed by means of the Arrhenius equation (7,18).

The Arrhenius equation is

$$k = se^{-E_a/RT}$$

where k is the rate constant, T is the absolute temperature, R is the universal gas constant, s is a constant called the frequency factor, and E_a is the energy of activation. The factor $e^{-E_a/RT}$ is the fraction of molecules having energy E_a or greater. The energy of activation or E_a is the excess over the average energy that reactants must have for the reaction to take place.

From the above equation it can be seen that a plot of ln k vs. 1/T will yield a straight line with a slope of $-E_a/R$ and an intercept of ln s. These plots were made where possible and the corresponding energies of activation obtained.

D. Multiple Regression

When data does not correspond to accepted theory, it is often necessary and convenient to resort to other methods of analysis. One method used more and more is the statistical approach through multiple regression (4,10,16).

In using multiple regression we assume that some observation Y is expressible as a function of some known or controllable variables X_1, X_2, -------, X_k, say, with residual errors e_i which are normally and independently distributed around a mean of zero and a constant variance of σ^2, e.g., $e_i \sim NID(0,\sigma^2)$. For example, in this study the observed value Y, the conversion, was expressed as both linear and quadratic functions of the process variables space velocity, temperature, and initial

nitrogen concentration. The model under the linear assumption is

$$Y_i = B_0 + B_1X_{1i} + B_2X_{2i} + B_3X_{3i} + e_i$$

where the $e_i \sim NID(0, \sigma^2)$, Y_i is the conversion at the ith level, X_{1i} the temperature, X_{2i} the space velocity, and X_{3i} the initial concentration of nitrogen at the ith level.

For a fixed X_2 and X_3, the above model could be rewritten as

$$(Y_i - B_2X_2 - B_3X_3) = B_0 + B_1X_{1i} + e_i$$

or

$$Y_{iadj.} = B_0 + B_1X_{1i} + e_i$$

where the $Y_{iadj.}$ is now seen to be linear with respect to X_1. This same analogy could be used to show linearity with respect to X_2 and X_3 with X_1, X_3 and X_1, X_2 held constant respectively. To estimate the B's and σ^2 in the above model, we use the method of maximum likelihood (4). The likelihood function is

$$L = \left(\frac{1}{2\pi\sigma^2}\right)^{n/2} e^{-\frac{1}{2\sigma^2}\sum_{i=1}^{n}(Y_i - B_0 - B_1X_{1i} - B_2X_{2i} - B_3X_{3i})^2}$$

The maximum likelihood estimators of the B's and σ^2 are those estimators which minimize L of 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, B_3, and σ^2 and equating these partials to zero. Those values of B_0, B_1, B_2, B_3, and σ^2 which satisfy the equations are said to be the maximum likelihood estimators of the above parameters. These estimators are written as b_0, b_1, b_2, b_3, and $\hat{\sigma}^2$ respectively.

Performance of the above yields equations of estimation for calculating the estimators.

This procedure was carried out in this study for both the linear and quadratic models and the estimators obtained. The actual calculations were done on an IBM 650 computer.

Certain statistical hypotheses may be tested regarding the models used. Where possible the tests of hypotheses were made and the analysis of variance tables constructed.

V DISCUSSION OF RESULTS

A. Exploratory Runs

A number of exploratory runs were made to determine a suitable range of operating conditions. We were interested in determining the effect of changing operating conditions during a given run, finding a suitable hydrogen flow rate, and determining a satisfactory temperature range.

Run R-12, made with a hydrogen flow rate of 500 SCF/bbl, shows the type of data obtained when the process variable space velocity is varied during a given run. The data are given in Table V. It appears from the conversions shown that the catalyst was deactivating rapidly. For example, the conversion at a space velocity of 4.0 was 0.268 at the beginning of the run and 0.118 at the end of the run. A later run, however, made with a hydrogen flow rate of 7500 SCF/bbl and more severe conditions, indicated that catalyst deactivation was negligible. The results of this run, R-16, are shown in Table VI. It can be seen that the conversion here remained reasonably constant at 0.950. From these results it appeared that either at low hydrogen rates the catalyst deactivated rapidly or that changing space velocity during a run "upset" the catalyst. Therefore, it was decided to run with a hydrogen flow rate of 7500 SCF/bbl and to change space velocity a maximum of once during a run.

In order to determine whether 7500 SCF/bbl was substantially above some critical flow rate, runs R-19 and R-20 were made. Run R-19 was made at 7500 SCF/bbl, run R-20 at 5000 and 2500 SCF/bbl. The data from these runs are tabulated in Table VII. The results were:

Hydrogen Flow Rate	Conversion
7500	0.649
5000	0.649
2500	0.612

It can be seen from these results that 7500 SCF/bbl is well above a critical flow rate.

The temperature range was decided upon from previous work done at Montana State College for Esso Research and Engineering Company (6) and by Ryffel (17).

Before the temperature range of 675 to 775°F and hydrogen flow rate of 7500 SCF/bbl had been decided upon, several runs (R-1,3,5,10,12) had been made using pyrrole in various diluents. The data and operating conditions for these runs are included in Tables VIII through XII for future reference only.

During the preliminary investigation it was found that at temperatures of 700°F and above part of the product from the destructive hydrogenation of pyrrole was insoluble in n-heptane. In order to minimize equipment difficulties, it was decided to use no more pyrrole-n-heptane feeds.

B. Conversion-Time Study

Run R-16 was made at severe conditions in order to determine the maximum time to run after line-out before sampling. The data are tabulated in Table VI and the plot of conversion vs. line-out time is shown in Figure 3. These data indicated a maximum line-out time of about twelve hours.

C. Test For Diffusion

Ryffel (17) and Mahugh (13) have shown diffusion not to be controlling; therefore, only one check run was made for verification. Run R-16 was made at 725°F, a space velocity of 0.50, and with a charge of 50 grams of catalyst. Run R-17 was made at the same conditions except that the catalyst charge was 75 grams. The results of R-17 are given in Table XIII. The conversion from R-16 was 0.944 and that for R-17 was 0.941. This indicated that diffusion was not controlling. It was also noted from the results of runs R-19 and R-20 that varying the hydrogen flow rate from 5000 to 7500 SCF/bbl had no effect on the conversion. This also indicated that diffusion was not controlling.

D. Empirical Rate Equation

A series of runs using pyridine in toluene was made at varying space velocities and temperatures in order to determine an empirical rate equation. The data from these runs are listed in Table XIV. These data were plotted in Figure 4 as $\ln(C_o/C_o-x)$ vs. 1/SV. A plot of $\ln(C_o/C_o-x)$ vs. 1/SV will yield a straight line if the reaction is first order. It is seen that the assumption of first order fits the data very well in the 675 to 725°F range. The method of least squares was used to calculate the slopes of the straight lines. These values are tabulated in Table XV. The slopes of these lines are the reaction rate constants at the respective temperatures. For example, the reaction rate constant for the destructive hydrogenation of pyridine in toluene at 675°F was calculated as 0.375 hr^{-1}.

Another series of runs was made, again using a pyridine-toluene feed. These runs were made specifically for obtaining data for multiple regression analysis, but it was found that enough data at 675°F were available for determining the first order reaction rate constant at various initial nitrogen concentrations. The data from these runs are tabulated in Table XVI, and the calculated reaction rate constants are listed in Table XVII. Figure 5 is a plot showing the effect of initial concentration on the reaction rate constant for pyridine in toluene. It can be seen that in the range studied the reaction rate constant increases quite rapidly as the initial nitrogen concentration decreases.

A series of runs was also made using pyrrole-toluene feeds. These runs were made with the two-fold purpose of obtaining an empirical rate equation and of using the data in a multiple regression analysis. The data from these runs are tabulated in Tables XVIII and XIX. These data were plotted assuming a first order reaction. A typical plot is shown in Figure 6. Since this curve had a definite downward trend, the data were plotted assuming a second order reaction. A plot of $1/(C_o-x)$ vs. $1/SV$ will yield a straight line if the reaction is of second order. This plot of $1/(C_o-x)$ vs. $1/SV$ is shown in Figure 7 with the same data as that used for Figure 6. It appeared that these data correlated very well with the assumption of a second order reaction. The pyrrole-toluene data were all plotted assuming a second order reaction. It was found that at space velocities less than 1, the data no longer approximated a straight line. Therefore, only those data obtained at space velocities

of 1 or greater were used in determining the reaction rate constants. These data are shown in Figures 8-13. The corresponding second order reaction rate constants were calculated by the method of least squares and the results tabulated in Table XX. Figure 14 is a plot showing the effect of initial concentration on the reaction rate constant for the destructive hydrogenation of pyrrole in toluene. It was noted that in the range studied, the reaction rate constant increased rapidly as the initial nitrogen concentration decreased. From the results plotted in Figures 5 and 14, it can be seen that the effect of initial nitrogen concentration on the reaction rate constant was quite similar for both pyridine and pyrrole.

E. Energy of Activation

The energies of activation were calculated using the Arrhenius equation. This energy, E_a, was obtained by plotting ln k versus 1/T for both the pyrrole in toluene and pyridine in toluene. This plot should yield a straight line with a slope of $-E_a/R$ and an intercept of ln s. The plots are shown in Figures 15 and 16. The energies of activation were calculated for the six initial concentrations for pyrrole and averaged. The results are tabulated in Table XXI. The calculated energy of activation for pyridine in toluene was 10,200 cal/mole and that for pyrrole in toluene was 16,890 cal/mole. These values are valid for the temperature range of 675 to 725°F with the restriction on the space velocity formerly mentioned regarding pyrrole (SV = 1 and up).

F. Effect of Diluent

As previously mentioned, the hydrogenation product of pyrrole was insoluble in n-heptane, therefore it was decided not to study pyrrole-n-heptane feeds.

A feed containing pyrrole in methylcyclohexane was run at various space velocities. The data obtained from these runs are tabulated in Table XXII. These data were plotted, for comparison purposes only, assuming a second order reaction. The plot is shown in Figure 17 along with the data for pyrrole in toluene at 725°F. This plot indicated that the effect of diluent here was only slight. Since pyrrole-n-heptane feeds were not used and the difference in effects between pyrrole-toluene feeds and pyrrole-methylcyclohexane feeds was not large, it was decided to make no further diluent studies involving pyrrole.

Several runs were made using pyridine in various diluents. The data obtained from pyridine-n-heptane feeds are listed in Table XXIII. These data are plotted in Figures 18-20, assuming a first order reaction, for comparison with pyridine-toluene feeds. From these figures it was seen that the effect of diluent on hydrogenation of pyridine was very significant. The series of runs made with pyridine in methylcyclohexane also indicated that the diluent had a significant effect. The data from the pyridine-methylcyclohexane runs are listed in Table XXIV. The data obtained at 675°F from the runs using pyridine-toluene, pyridine-n-heptane, and pyridine-methylcyclohexane are plotted in Figure 21 assuming a first order reaction. It appeared from the results that the paraffinic diluent

allowed the greatest overall nitrogen conversion while the aromatic allowed the least. In order to substantiate these results, it was decided to use a diluent having both paraffinic and aromatic properties. This could be checked by two methods:

(1) Mixing an aromatic and paraffin

(2) Selecting an aromatic with a paraffin group attached

Both methods were checked.

The first method (1) was checked by mixing a feed containing 39 weight per cent n-heptane and 61 weight per cent toluene before adding the pyridine. This feed was run at a constant temperature of 725°F and space velocities of 2, 4, and 1/2. The results of these runs are tabulated in Table XXV. For a quick check we may look at the conversions at 725°F and a space velocity of 4. They were as follows:

in n-heptane	0.553
in mixture	0.243
in toluene	0.176

It is readily seen that the data checks. Another run was made, this time using a feed containing 65 weight per cent n-heptane and 35 weight per cent toluene. This run was also made at a temperature of 725°F and a space velocity of 4. The conversion is listed below along with the above results in descending order

diluent	conversion
n-heptane (C_7)	0.553
65 Wt.% C_7	0.350
39 Wt.% C_7	0.243
toluene	0.176

Thus it appeared that mixtures of aromatics and paraffins behaved as predicted.

The second (2) method was checked by making several runs with cumene (isopropylbenzene) at 725°F and various space velocities. The results of these runs are given in Table XXVI. The data from the pyridine in toluene, n-heptane, methylcyclohexane, and cumene runs at 725°F are plotted in Figure 22 assuming a first order reaction. These data indicated that the paraffinic diluent definitely resulted in better overall nitrogen conversion.

The effect of diluent shown above is probably due to the relative adsorptivities of the respective diluents on solid materials such as carbon, molybdenum sulfide, and silica compounds. The literature (3,5, 12) reports that aromatics are more highly adsorbed than naphthenics and that naphthenics in turn are more highly adsorbed than paraffinics. If toluene was highly adsorbed on the catalyst, the number of active sites available to pyridine would be small. By the same analogy, if heptane is not highly adsorbed, the number of active sites available would be greater. This appears to be a reasonable explanation of the diluent effect shown above. This also indicates that the surface reaction is the controlling reaction in the destructive hydrogenation of pyridine, assuming no interaction between pyridine and the diluent used.

G. Multiple Regression of Conversion on Temperature, Initial Concentration, and Space Velocity

The data obtained from the destructive hydrogenation of pyrrole and pyridine in toluene were used to estimate the parameters of the linear and

quadratic models postulated and to test hypotheses about these models. The nomenclature used was as follows:

Y - overall nitrogen conversion, x/C_o
X_1 - temperature, °R (°F + 460)
X_2 - initial nitrogen concentration, C_o
X_3 - space velocity, v/v/hr (SV)
X_4 - 1/SV, hr

It was assumed that the conversion could be expressed as both linear and quadratic functions of various groupings of the above process variables (X).

The linear models used were

$$Y_i = B_o + B_1X_{1i} + B_2X_{2i} + B_3X_{3i} + e_i$$

and

$$Y_i = B_o + B_1X_{1i} + B_2X_{2i} + B_4X_{4i} + e_i$$

$$e_i \sim NID(0, \sigma^2)$$

while the corresponding quadratic models were

$$Y_i = B_o + B_1X_{1i} + B_2X_{2i} + B_3X_{3i} + B_{11}X_{1i}^2 + B_{22}X_{2i}^2 + B_{33}X_{3i}^2 + B_{12}X_{1i}X_{2i} + B_{13}X_{1i}X_{3i} + B_{23}X_{2i}X_{3i} + e_i$$

and same as above with subscript 3 replaced by 4.

The data used for estimating the B's in the above expressions are tabulated in Tables XIV, XVI, XVIII, and XIX. The B's were estimated by the method of maximum likelihood, the calculations being done on an IBM 650 computer.

When working with the eight different equations used, the following notation was adopted:

Y_i (case I) - linear model for pyrrole in toluene with variables X_1, X_2, X_3

Y_i (case II) - linear model for pyrrole in toluene with variables X_1, X_2, X_4

Y_i (case III) - quadratic model for pyrrole in toluene with variables X_1, X_2, X_3

Y_i (case IV) - quadratic model for pyrrole in toluene with variables X_1, X_2, X_4

Y_i (case V) - linear model for pyridine in toluene with variables X_1, X_2, X_3

Y_i (case VI) - linear model for pyridine in toluene with variables X_1, X_2, X_4

Y_i (case VII) - quadratic model for pyridine in toluene with variables X_1, X_2, X_3

Y_i (case VIII) - quadratic model for pyridine in toluene with variables X_1, X_2, X_4

The estimates of the B's, b's, are listed for cases I-IV in Table XXVII and for cases V-VIII in Table XXVIII. To illustrate the results obtained, one equation is written out in final form as

$$Y(\text{case VI}) = -3.7296 + 0.0035167X_1 - 0.21591X_2 + 0.30244X_4$$

where the estimators have been rounded off to five significant figures. In order to examine further the equation, we will calculate the conversion at a set of operating conditions and compare this result to the actual conversion obtained. For example, at

$$X_1 = 700°F = 1160°R$$
$$X_2 = 1.0 \text{ Wt.\% N}$$
$$X_3 = 1/SV = 1/1 = 1$$

the predicted conversion is 0.436 while the actual conversion taken from Table XIV is 0.548. Therefore, it appears that the linear model is a

fairly good estimator. At the same conditions mentioned above, the quadratic equation, Y(case VII), yields a conversion of 0.475. It can be seen that this is even closer to the actual conversion (0.548) than the value from the linear model (0.436).

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

$$H; \quad B_1 = B_2 = B_3 = 0$$
$$B_1 = B_2 = B_4 = 0$$

for the linear models.

These tests were conducted for each of the four linear models, and in each case the hypothesis was rejected. The analysis of variance tables used for the above tests are included in Tables XXIX-XXXII in the Appendix. Had the multiple regression data been obtained from orthogonal designs, the hypotheses

$$H; \quad B_i = 0 \quad \text{for } i = 1, 2, \text{ or } 3$$

could have been tested also.

Another series of hypotheses tested were the hypotheses for the quadratic models

$$H; \quad B_{11} = B_{22} = B_{33} = B_{12} = B_{13} = B_{23} = 0$$

From the results of such a test we can decide whether the quadratic terms are essential in the models.

The analysis of variance tables for the quadratic models and the tests of the above hypotheses are included in Tables XXXIII-XXXVI. It was decided from the results that the models for cases I, IV, VII, VIII were to be used for the equations of estimation.

VI SUMMARY AND CONCLUSIONS

The destructive hydrogenation of pyrrole in toluene appears to be a pseudo second order reaction. This observation is valid for a temperature range of 658 to 741°F and a space velocity range of 1.0 to 8.0. For space velocities less than 1.0, the reaction is no longer second order and appears to be of no simple order.

The energy of activation for pyrrole as calculated from the Arrhenius equation was found to be 16,890 cal/mole.

Multiple regression analysis of the destructive hydrogenation of pyrrole in toluene indicates that the conversion may be predicted by a linear function of the temperature, space velocity, and the initial nitrogen concentration. It was also found that the conversion may be predicted by a quadratic function of the temperature, initial nitrogen concentration, and reciprocal space velocity.

Preliminary investigations showed hydrogenation products of pyrrole produced at temperatures of 700°F and above were insoluble in n-heptane. Therefore, an extensive diluent study was not conducted on pyrrole.

The destructive hydrogenation of pyridine in toluene appears to be a pseudo first order reaction in the temperature range of 675 to 725°F and a space velocity range of 1/2 to 4. Above 725°F the reaction no longer appears to be first order or any other simple order.

The energy of activation for pyridine as calculated from the Arrhenius equation was found to be 10,200 cal/mole.

Multiple regression analysis of the destructive hydrogenation of pyridine in toluene indicates that the conversion may be predicted by a quadratic function of the temperature, space velocity, and the initial nitrogen concentration. The conversion may also be predicted by a quadratic function of the temperature, initial nitrogen concentration, and reciprocal space velocity.

The type of diluent with pyridine in destructive hydrogenation had a marked effect on the conversion. The conversion of pyridine was greatest when a paraffinic diluent was used and least when an aromatic was used. It was also shown that a naphthenic diluent gives conversions in the zone between paraffins and aromatics. The diluents studied included toluene, cumene, methylcyclohexane, and n-heptane.

It was found that for both compounds an increase in temperature caused an increase in conversion, and a decrease in space velocity caused an increase in conversion. For the initial concentration range studied (0.2 to 2.0 Wt.% N), the reaction rate constants were found to increase quite rapidly as the initial nitrogen concentration was decreased.

The calculations leading to the above observations are based on overall nitrogen concentrations.

In case of further studies along the lines mentioned above, I would recommend a series of studies using feeds containing both pyrrole and pyridine. It would be interesting to know if the compounds behave the same in a mixture as when handled alone.

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VIII LITERATURE CITED

(1) Ball, J. S., et al., "Composition of Colorado Shale-Oil Naphtha", Ind. and Engr. Chem., 41:581 (1949).

(2) Ball, J. S., et al., "Nitrogen Content of Crude Petroleum", Ind. and Engr. Chem., 43:25 (1951).

(3) Ballow, E. V., and Sydney Ross, "The Adsorption of Benzene and Water Vapor by Molybdenum Sulfide", J. Phys. Chem., 57:653 (1953).

(4) Brunk, H. D., "An Introduction to Mathematical Statistics", Ginn and Company, New York, (1960).

(5) Cines, M. R., and F. N. Ruehlen, "Selective Adsorption-2,4 Dimethylpentane-Benzene-Silica Gel at 65.6°", J. Phys. Chem., 57:710 (1953).

(6) Currie, R. A., M.S. Thesis, Montana State College, (1960).

(7) Glasstone, S., "Thermodynamics for Chemists", D. Van Nostrand Company, Inc., New Jersey, (1947).

(8) Hirst, L. L., and C. C. Chaffee, "Liquid Fuel From Coal", Ind. and Engr. Chem., 42:1607 (1950).

(9) Hodgeman, C. D., and H. N. Holmes, "Hand Book of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, (1953).

(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", Analytical Chem., 22:354 (1950).

(12) Kiselev, A. V., and V. V. Platova, "Adsorption of Toluene-Heptane Mixture by Oxidized and Graphitized Carbon", M. V. Lomonosov State University, Moscow. (Chem. Abstracts, 1957).

(13) Mahugh, R. A., Ph.D. Thesis, Montana State College (1960).

(14) McKee, A. F., M.S. Thesis, Montana State College, (1956).

(15) Mills, G. A., et al., "Chemical Characteristics of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion.", J. Amer. Chem. Soc., 72:1544 (1950).

(16) Ostle, B., "Statistics in Research", Iowa State Press, Ames, Iowa, (1954).

(17) Ryffel, J. R., Ph.D. Thesis, Montana State College, (1960).

(18) Smith, J. M., "Chemical Engineering Kinetics", McGraw-Hill Book Co., New York, (1956).

(19) Staff Report, "Carbide Takes the Hex Out of Coal", Chem. Engr. News, 30:1954 (1952).

(20) Stanfield, K. E., and H. M. Thorne, "Oil-Shale Research and Process Development", Ind. and Engr. Chem., 43:20 (1951).

(21) Storch, H. H., and R. C. Grass, "Coal-to-Oil Research at Bruceton, Pa.", Chem. Engr. News, 28:646 (1950).

(22) Storch, H. H., et al., "Hydrogenation of Bituminous Coal in Experimental Flow Plant", Ind. and Engr. Chem., 42:83 (1950).

(23) Storch, H. H., et al., "Hydrogenation of Coal in a Fluidized Bed", Ind. and Engr. Chem., 42:861 (1950).

IX APPENDIX

Thermodynamic Study

A thermodynamic study of the following overall reactions was performed at four pressures and four temperatures.

pyridine + $5H_2$ (hydrogen) $\longrightarrow$ $CH_3(CH_2)_3CH_3$ (n-pentane) + NH_3 (ammonia)

pyrrole + $3H_2$ (hydrogen) $\longrightarrow$ $CH_3(CH_2)_2CH_3$ (n-butane) + NH_3 (ammonia)

The data required for the calculations are given in Table I. Some of the data was readily available from handbooks while the rest was estimated. When more than one method of estimation was used, the results were averaged.

The equations used for calculations are as follows:

$$\Delta H^\circ_{298} = \Delta H^\circ_{f\ 298(\text{products})} - \Delta H^\circ_{f\ 298(\text{reactants})}$$

$$S^\circ_{298} = S^\circ_{298(\text{products})} - S^\circ_{298(\text{reactants})}$$

$$\Delta F_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

$$T_{NE} = \Delta H^\circ_{NE}/\Delta S^\circ_{NE}$$

$$\ln K_{eq} = -\Delta F^\circ/_{RT}$$

The free energy changes and equilibrium constants at four temperatures are given in Table II.

Other equations used are given below:

$$\ln\gamma = \frac{9}{128}\left(\frac{PT_c}{TP_c}\right)\left[1 - 6\left(\frac{T_c}{T}\right)^2\right]$$

$$K_N = K_{eq.}\ P^{\Delta n}/K_\gamma$$

Δn = moles of reactants - moles of products

$$K_\gamma = \frac{\gamma_{NH_3}\gamma_{C_5}}{(\gamma_H)^5\ \gamma_{pyridine}}$$

$$K_\gamma = \frac{\gamma_{NH_3}\ \gamma_{C_4}}{(\gamma_H)^3\ \gamma_{pyrrole}}$$

The calculated activity coefficients, γ, are given in Table III and the Conversions in Table IV.

TABLE I

THERMODYNAMIC DATA

Compound	T_c (°K)	P_c (atm)	$\Delta H^\circ_{f\ 298}$ cal/mole	S°_{298} (eu/mole)
Ammonia	405	111.5	-11,030	46.03
Hydrogen	33	12.8		31.21
Pyrrole	640	61.7	31,100	65.61
Pyridine	617	60.0	27,540	68.90
n-Butane	426	36.0	-29,810	74.50
n-Pentane	470	33.0	-35,000	83.40

TABLE II

FREE ENERGY CHANGES AND EQUILIBRIUM CONSTANTS

Temp (°K)	ΔF° (cal/mole) Pyrrole	ΔF° (cal/mole) Pyridine	K_{eq} Pyrrole	K_{eq} Pyridine
300	-60,420	-45,120	5.5×10^{43}	5.0×10^{32}
500	-52,620	-23,160	7.5×10^{22}	1.2×10^{10}
700	-44,890	80	8.3×10^{13}	1.06
1000	-33,230	27,870	1.7×10^{7}	5.8×10^{-9}

TABLE III

ACTIVITY COEFFICIENTS

Press (atm)	Temp (°K)	γ_H	γ_{NH_3}	γ_{C_5}	γ_{C_4}	$\gamma_{Pyridine}$	$\gamma_{Pyrrole}$
1	300	1.000	0.994	0.941	0.970	0.945	0.941
	500	1.000	1.000	0.990	0.994	0.991	0.992
	700	1.000	1.000	0.999	0.998	0.999	0.998
	1000	1.000	1.000	1.000	1.000	1.000	1.000
10	300	1.000	0.920	0.531	0.735	0.556	0.533
	500	1.000	0.987	0.890	0.946	0.891	0.882
	700	1.000	0.999	0.968	0.986	0.964	0.962
	1000	1.000	1.000	0.997	0.999	0.990	0.991
50	300	1.003	0.656	0.042	0.214	0.053	0.0427
	500	1.002	0.930	0.553	0.751	0.556	0.530
	700	1.001	0.984	0.845	0.929	0.830	0.815
	1000	1.000	1.000	0.981	0.996	0.955	0.950
200	300	1.011	0.185	3.2×10^{-6}	0.0029	7.8×10^{-6}	3.32×10^{-6}
	500	1.007	0.742	0.093	0.329	0.0952	0.079
	700	1.005	0.925	0.510	0.749	0.470	0.439
	1000	1.004	1.000	0.916	0.986	0.831	8.12

TABLE IV

THERMODYNAMIC RESULTS

Press (atm)	Temp °F	K_{eq} Pyrrole (1)	K_{eq} Pyridine (2)	K_{γ} (1)	K_{γ} (2)	K_N (1)	K_N (2)	% Conversion (1)	% Conversion (2)
1	300	5.5×10^{43}	5.0×10^{32}	1.025	0.990	5.36×10^{43}	5.1×10^{32}	99.9	99.9
	500	7.5×10^{22}	1.2×10^{10}	1.001	0.991	7.5×10^{22}	1.21×10^{10}	99.9	99.2
	700	8.3×10^{13}	1.06	1.000	0.999	8.3×10^{13}	1.06	99.9	48.2
	1000	1.7×10^{7}	5.8×10^{-9}	1.000	1.000	1.7×10^{7}	5.8×10^{-9}	99.1	0.1
10	300	1.7×10^{7}	5.8×10^{-9}	1.268	0.877	4.35×10^{45}	5.7×10^{36}	99.9	99.9
	500	1.7×10^{7}	5.8×10^{-9}	1.059	0.987	7.09×10^{24}	1.21×10^{14}	99.9	99.7
	700	1.7×10^{7}	5.8×10^{-9}	1.023	1.002	8.12×10^{15}	1.06×10^{4}	99.9	90.5
	1000	1.7×10^{7}	5.8×10^{-9}	1.008	1.007	1.68×10^{9}	5.75×10^{-5}	99.7	1.2
50	300	1.7×10^{7}	5.8×10^{-9}	3.262	0.516	4.22×10^{46}	6.05×10^{39}	99.9	99.9
	500	1.7×10^{7}	5.8×10^{-9}	1.310	0.920	1.43×10^{26}	8.15×10^{16}	99.9	99.9
	700	1.7×10^{7}	5.8×10^{-9}	1.118	0.997	1.86×10^{17}	6.61×10^{6}	99.9	96.8
	1000	1.7×10^{7}	5.8×10^{-9}	1.049	1.028	4.06×10^{10}	3.53×10^{-2}	99.8	19.9

TABLE IV (continued)

THERMODYNAMIC RESULTS

Press (atm)	Temp °K	K_{eq} Pyrrole (1)	K_{eq} Pyridine (2)	K_{γ} (1)	K_{γ} (2)	K_N (1)	K_N (2)	% Conversion (1)	% Conversion (2)
200	300	1.7×10^{7}	5.8×10^{-9}	156.5	0.0717	1.41×10^{47}	1.12×10^{43}	99.9	99.9
	500	1.7×10^{7}	5.8×10^{-9}	3.025	0.707	9.92×10^{26}	2.72×10^{19}	99.9	99.9
	700	1.7×10^{7}	5.8×10^{-9}	1.552	0.978	2.14×10^{18}	1.73×10^{9}	99.9	98.8
	1000	1.7×10^{7}	5.8×10^{-9}	1.200	1.078	5.6×10^{11}	8.62	99.9	64.1

TABLE V

EFFECT OF VARYING SPACE VELOCITY DURING A GIVEN RUN (R-13)

Sample No.	Space Velocity	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o
1	4	0.765	0.732	0.268
2	4	0.775	0.740	0.260
3	10	0.926	0.883	0.117
4	10	0.926	0.883	0.117
5	7	0.927	0.884	0.116
6	7	0.934	0.892	0.108
7	2	0.870	0.832	0.168
8	2	0.880	0.840	0.160
9	4	0.922	0.881	0.119
10	4	0.924	0.882	0.118

Uniform Operating Conditions:

Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 500 SCF/bbl
Initial Nitrogen: 1.047 Wt.% N from pyrrole
Diluent: 42 Wt.% n-Heptane
58 Wt.% Toluene
Weight of Catalyst: 20 gms

TABLE VI

CATALYST DEACTIVATION AND LINE-OUT TIME STUDY (R-16)

Sample No.	Hours Line-out	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o
1	0	0.0238	0.0262	0.974
2	2	0.0133	0.0146	0.985
3	4	0.0174	0.0192	0.981
4	6	0.0146	0.0161	0.984
5	8	0.0163	0.0180	0.982
6	10	0.0506	0.0558	0.944
7	12	0.0383	0.0422	0.958
8	15	0.0513	0.0565	0.944
9	18	0.0636	0.0700	0.930
10	21	0.0500	0.0551	0.945
11	24	0.0658	0.0725	0.927
12	27	0.0472	0.0519	0.948
13	29	0.0643	0.0707	0.929

Uniform Operating Conditions:

Pressure: 250 psig
Temperature: 725°F
Space Velocity: 0.5 cc/cc per hour
Hydrogen Rate: 7500 SCF/bbl
Initial Nitrogen: 0.909 Wt.% N from pyrrole
Diluent: Methylcyclohexane
Weight of Catalyst: 50 gms

TABLE VII

CRITICAL HYDROGEN FLOW RATE STUDY
(R-19, 20)

Hydrogen Rate (SCF/bbl)	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o	C_o
7500	0.338	0.351	0.649	0.964
5000	0.335	0.351	0.649	0.954
2500	0.370	0.388	0.612	0.954

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Initial Nitrogen: (above) from pyrrole
Diluent: Methylcyclohexane
Weight of Catalyst: 20 gms
Space Velocity: 4.0 cc/cc per hour

TABLE VIII

PYRROLE-n-HEPTANE, 555°F, 185 psig
(R-1)

Sample No.	Space Velocity	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o
1	7	0.710	0.727	0.273
2	2	0.515	0.527	0.473
3	20	0.861	0.882	0.118

Uniform Operating Conditions:
Pressure: 185 psig
Temperature: 555°F
Hydrogen Rate: 500 SCF/bbl
Initial Nitrogen: 0.978 Wt.% N from Pyrrole
Diluent: n-Heptane
Weight of Catalyst: 10 gms

TABLE IX

PYRROLE-n-HEPTANE, 650°F, 185 psig
(R-3)

Sample No.	Space Velocity	$C_o - x$	$C_o - x$	x/C_o
1	7	0.515	0.528	0.472
2	2	0.330	0.338	0.662
3	20	0.722	0.738	0.262

Uniform Operating Conditions:
Pressure: 185 psig
Temperature: 650°F
Hydrogen Rate: 500 SCF/bbl
Initial Nitrogen: 0.978 Wt.% N from Pyrrole
Diluent: n-Heptane
Weight of Catalyst: 10 gms

TABLE X

PYRROLE-n-HEPTANE, 555°F, 250 psig
(R-5)

Sample No.	Space Velocity	$C_o - x$	$C_o - x$	x/C_o
1	7	0.742	0.758	0.242
2	20	0.864	0.883	0.117
3	2	0.701	0.718	0.282

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 555°F
Hydrogen Rate 500 SCF/bbl
Initial Nitrogen: 0.978 Wt.% N from Pyrrole
Diluent: n-Heptane
Weight of Catalyst: 10 gms

TABLE XI

PYRROLE IN TOLUENE, EXPLORATORY
(R-10)

Sample No.	Space Velocity	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o
1	4	0.586	0.563	0.437
2	10	0.868	0.837	0.163
3	7	0.823	0.792	0.208

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 500 SCF/bbl
Initial Nitrogen: 1.04 Wt.% N from Pyrrole
Diluent: Toluene
Weight of Catalyst: 20 gms

TABLE XII

PYRROLE IN 50/50 TOLUENE, METHYLCYCLOHEXANE, EXPLORATORY
(R-12)

Sample No.	Space Velocity	$C_o - x$	$C_o - x$	x/C_o
1	4	0.909	0.870	0.130
2	10	0.956	0.913	0.087
3	7	0.963	0.921	0.079
4	2	0.797	0.763	0.237
5	4	0.930	0.889	0.111

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 500 SCF/bbl
Initial Nitrogen: 1.046 Wt.% N from Pyrrole
Diluent: 50 Wt.% Toluene, 50 Wt.% Methylcyclohexane
Weight of Catalyst: 20 gms

TABLE XIII

TEST FOR DIFFUSION (R-17)

Sample	$C_o - x$	$\frac{C_o - x}{C_o}$	x/C_o
1	0.0328	0.0361	0.964
2	0.0538	0.0593	0.941

Uniform Operating Conditions:

Pressure: 250 psig
Temperature: 725°F
Space Velocity: 0.50 cc/cc per hour
Hydrogen Rate: 7500 SCF/bbl
Initial Nitrogen: 0.909 Wt.% N from Pyrrole
Diluent: Methylcyclohexane
Weight of Catalyst: 75 gms

TABLE XIV

EMPIRICAL RATE DATA FOR PYRIDINE IN TOLUENE

Temp °F	Space Velocity	C_o	C_o-x	$C_o/(C_o-x)$	ln $C_o/(C_o-x)$	1/SV	Wt. Catalyst
725	0.5	1.044	0.248	4.22	1.44	2.00	75
725	2.0	1.043	0.710	1.472	0.386	0.50	20
725	4.0	1.032	0.850	1.215	0.195	0.25	20
675	0.5	1.035	0.487	2.13	0.755	2.00	75
675	2.0	0.991	0.821	1.205	0.1865	0.50	20
675	1.0	0.987	0.686	1.439	0.364	1.00	50
750	2.0	0.999	0.554	1.803	0.590	0.50	20
750	4.0	1.004	0.747	1.344	0.295	0.25	20
750	1.0	0.987	0.227	4.35	1.47	1.00	50
750	0.5	0.991	0.031	31.90	3.46	2.00	75
700	2.0	0.996	0.753	1.323	0.279	0.50	20
700	0.5	1.000	0.347	2.89	1.060	2.00	75
700	1.0	0.998	0.577	1.732	0.548	1.00	50
700	4.0	0.981	0.828	1.184	0.169	0.25	20
775	1.0	0.984	0.069	14.13	2.65	1.00	50
775	4.0	0.985	0.645	1.525	0.422	0.25	20
775	2.0	1.023	0.453	2.26	0.815	0.50	20
775	0.5	1.037	0.000			2.00	75

Uniform Operating Conditions:

Pressure: 250 psig
Hydrogen Rate: 7500 SCF/bbl
Initial Nitrogen: Approximately 1.0 Wt.% N from Pyridine
Diluent: Toluene

TABLE XV

REACTION RATE CONSTANTS FOR PYRIDINE IN TOLUENE
(C_o-1)

Temp °F	Temp °R	Rate Constant	ln k	1/°R 10^3
675	1135	0.375	-0.982	0.881
700	1160	0.5375	-0.622	0.863
725	1185	0.726	-0.321	0.844

TABLE XVI

PYRIDINE IN TOLUENE DATA FOR MULTIPLE REGRESSION

Temp °F	Space Velocity	C_o	C_o-x	$\ln \frac{C_o}{C_o-x}$	x/C_o	1/SV
725	4.0	1.295	1.068	0.193	0.175	0.25
675	4.0	1.295	1.180	0.0935	0.088	0.25
675	2.0	0.515	0.384	0.294	0.254	0.50
675	4.0	0.518	0.477	0.1483	0.1375	0.25
775	2.0	1.303	0.580	0.810	0.555	0.50
675	4.0	1.990	1.896	0.0488	0.048	0.25
675	2.0	1.990	1.800	0.1015	0.095	0.50
725	4.0	1.990	1.772	0.115	0.108	0.25
775	4.0	1.313	0.932	0.343	0.290	0.25
675	4.0	0.204	0.150	0.302	0.261	0.25
675	2.0	0.204	0.099	0.717	0.512	0.50
700	2.0	0.204	0.057	1.272	0.721	0.50
725	2.0	1.302	0.920	0.348	0.293	0.50

Uniform Operating Conditions:
Pressure: 250 psig
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20 gms

TABLE XVII

REACTION RATE CONSTANTS AT 675°F FOR PYRIDINE IN TOLUENE

C_o	K	ln k
0.204	1.388	0.328
0.518	0.590	-0.528
1.000	0.375	-0.982
1.990	0.200	-1.612

TABLE XVIII

REACTION RATE AND MULTIPLE REGRESSION DATA FOR PYRROLE IN TOLUENE

Temp °F	Space Velocity	C_o	C_o-x	$\ln \frac{C_o}{C_o-x}$	$\frac{1}{C_o-x}$	Wt. of Catalyst
675	2	0.998	0.486	0.717	2.058	20
675	6	0.998	0.747	0.289	1.339	15
725	2	0.998	0.237	1.440	4.219	20
725	6	0.998	0.491	0.708	2.037	15
675	1	0.998	0.297	1.212	3.367	50
725	4	0.998	0.370	0.990	2.703	20
725	2	1.470	0.523	1.033	1.912	20
675	2.667	1.472	1.072	0.316	0.933	20
675	6	1.475	1.252	0.162	0.799	15
725	6	1.481	0.925	0.472	1.081	15
675	2	1.477	0.985	0.405	1.015	20
725	1	1.487	0.309	1.572	3.236	50
675	1	1.487	0.677	0.786	1.477	50
700	4	1.247	0.810	0.432	1.235	20
700	4	1.254	0.790	0.463	1.266	20
700	4	1.253	0.785	0.468	1.274	20
700	4	1.256	0.786	0.468	1.272	20
700	4	1.248	0.767	0.488	1.304	20
700	4	1.251	0.788	0.462	1.269	20

Uniform Operating Conditions:
Pressure: 250 psig
Hydrogen Flow Rate: 7500 SCF/bbl

TABLE XIX

REACTION RATE AND MULTIPLE REGRESSION DATA FOR PYRROLE IN TOLUENE

Temp °F	Space Velocity	C_o	C_o-x	$\ln \frac{C_o}{C_o-x}$	$\frac{1}{C_o-x}$	Wt. of Catalyst
658	4	1.252	1.034	0.192	0.9671	20
741	4	1.248	0.488	0.939	2.049	20
700	0.636	1.243	0.187	1.897	5.348	75
700	7.364	1.236	0.932	0.282	1.073	15
700	2	1.230	0.532	0.837	1.880	20
700	0.5	1.232	0.140	2.170	7.117	75
700	4	0.848	0.378	0.811	2.646	20
700	2	0.849	0.236	1.278	4.237	20
700	1	0.853	0.127	1.903	7.874	50
675	1	0.853	0.203	1.435	4.926	50
675	2	0.853	0.362	0.857	2.762	20
700	4	1.644	1.144	0.361	0.874	20
675	4	1.644	1.263	0.264	0.792	20
675	2	1.644	1.053	9.447	0.950	20
675	1	1.635	0.657	0.912	1.522	50
700	2	1.635	0.722	0.820	1.385	20
700	1	1.635	0.582	1.032	1.718	50
675	1	2.008	1.060	0.638	0.943	50
675	2	2.10	1.456	0.323	0.687	20
675	4	1.995	1.754	0.127	0.570	20
675	0.5	1.994	0.697	1.050	1.435	75
700	2	2.005	1.142	0.562	0.876	20
700	4	2.005	1.555	0.253	0.6431	20

Uniform Operating Conditions:
Pressure: 250 psig
Hydrogen Flow Rate: 7500 SCF/bbl

TABLE XX

SECOND ORDER REACTION RATE CONSTANTS FOR PYRROLE IN TOLUENE

C_o Wt.% N	Temp °F	Rate Constant	ln k
0.85	675	3.63	1.29
	700	6.55	1.88
1.00	675	2.31	0.837
	725	6.48	1.87
1.25	658	0.668	-0.403
	700	2.12	0.752
	741	4.997	1.609
1.48	675	0.768	-0.264
	725	2.535	0.932
1.64	675	0.689	-0.372
	700	1.190	0.174
2.00	675	0.4575	-0.782
	700	0.717	-0.333

TABLE XXI

ENERGIES OF ACTIVATION FOR PYRROLE IN TOLUENE

C_o Wt.% N	E_a Cal/mole
0.85	18,220
1.00	15,940
1.25	18,030
1.48	18,440
1.64	16,840
2.00	13,870
Ave.	16,890

TABLE XXII

DATA FROM DILUENT EFFECT RUNS FOR PYRROLE IN METHYLCYCLOHEXANE

Space Velocity	C_o	C_o-x	$\frac{C_o-x}{C_o}$	x/C_o	$\frac{1}{C_o-x}$
0.5	0.909	0.0538	0.0593	0.941	18.6
2.0	0.909	0.199	0.219	0.781	5.03
4.0	0.964	0.388	0.403	0.597	2.58

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20-50 gms

TABLE XXIII

DATA FROM DILUENT EFFECT RUNS FOR PYRIDINE IN n-HEPTANE

Space Velocity	Temp °F	C_o	C_o-x	$\frac{C_o}{C_o-x}$	$\ln \frac{C_o}{C_o-x}$	x/C_o
2	725	0.995	0.321	3.10	1.130	0.677
4	725	0.999	0.446	2.24	0.807	0.553
1	725	0.998	0.098	10.16	2.315	0.902
4	775	1.002	0.269	3.73	1.317	0.732
2	775	0.996	0.072	13.85	2.63	0.928
4	675	0.992	0.593	1.67	0.514	0.402
2	675	0.924	0.400	2.31	0.837	0.568
1	675	0.922	0.289	3.18	1.158	0.686

Uniform Operating Conditions:
Pressure: 250 psig
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20-50 gms

TABLE XXIV

DATA FROM DILUENT EFFECT RUNS
FOR PYRIDINE IN METHYLCYCLOHEXANE

Space Velocity	Temp °F	C_o	C_o-x	$\frac{C_o}{C_o-x}$	$\ln \frac{C_o}{C_o-x}$	x/C_o
1	675	0.993	0.452	2.195	0.787	0.544
2	675	0.965	0.508	1.896	0.640	0.472
4	675	0.994	0.680	1.463	0.381	0.316
0.5	725	0.977	0.031	31.5	3.45	0.968
2	725	0.972	0.416	2.335	0.848	0.572
4	725	0.974	0.577	1.685	0.522	0.406
1	775	0.993	0.166	5.97	1.786	0.832
2	775	0.962	0.229	4.20	1.435	0.762

Uniform Operating Conditions:
Pressure: 250 psig
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20-50 gms

TABLE XXV

DATA FROM DILUENT EFFECT RUNS FOR
PYRIDINE IN A TOLUENE (61 Wt.%) -n-HEPTANE (39 Wt.%)
MIXTURE

Space Velocity	C_o	C_o-x	$\frac{C_o}{C_o-x}$	$\ln \frac{C_o}{C_o-x}$	x/C_o
0.5	0.976	0.094	10.38	2.34	0.904
2	0.972	0.640	1.516	0.416	0.340
4	0.979	0.740	1.322	0.279	0.243

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20-75 gms

TABLE XXVI

DATA FROM DILUENT EFFECT RUNS FOR PYRIDINE IN CUMENE

Space Velocity	C_o	C_o-x	$\frac{C_o}{C_o-x}$	$\ln \frac{C_o}{C_o-x}$	x/C_o
0.5	0.980	0.114	8.59	2.15	0.884
1	0.983	0.337	2.92	1.07	0.657
2	0.978	0.536	1.826	0.602	0.452
4	0.976	0.672	1.452	0.372	0.312

Uniform Operating Conditions:
Pressure: 250 psig
Temperature: 725°F
Hydrogen Rate: 7500 SCF/bbl
Weight of Catalyst: 20-75 gms

TABLE XXVII

ESTIMATED COEFFICIENTS FOR REGRESSION MODELS, CASES I-IV

Estimator	Case I	Case II	Case III	Case IV
b_0	-4.5305332	-4.5394646	-2.3710898	-8.6234096
b_1	0.00487701	0.004476319	0.0003876363	0.01077451
b_2	-0.24320598	-0.24147541	0.49774896	-0.34850947
b_3	-0.093474257		-0.22474114	
b_4		0.34823998		1.0427255
b_{11}			0.0000024970204	-0.0000022873117
b_{22}			0.10609922	0.13600063
b_{33}			0.016026603	
b_{44}				-0.22563573
b_{12}			-0.00089065981	-0.00024832149
b_{13}			0.000022802535	
b_{14}				-0.00026176212
b_{23}			-0.0037247565	
b_{24}				0.026821470

TABLE XXVIII

ESTIMATED COEFFICIENTS FOR REGRESSION MODELS, CASES V-VIII

Estimator	Case V	Case VI	Case VII	Case VIII
b_0	-3.3133399	-3.7296289	-5.9198173	-2.7952237
b_1	0.0035861463	0.0035166951	0.0046639856	-0.00055022897
b_2	-0.18165883	-0.21590753	1.4866805	2.1007824
b_3	-0.13538590		0.41424504	
b_4		0.30244157		-0.098392148
b_{11}			0.000001466914	0.0000027386258
b_{22}			0.20014974	0.20889891
b_{33}			0.052824176	
b_{44}				-0.19171121
b_{12}			-0.0020106293	-0.0022653232
b_{13}			-0.00074290811	
b_{14}				0.0010917251
b_{23}			0.060894199	
b_{24}				-0.42370350

TABLE XXIX

ANALYSIS OF VARIANCE TABLE FOR TEST CASE I

Source	SS	d.f.	m.s.
SSR	1.54463	3	0.51487
SSE	0.16075	33	0.00487
SST	1.70538	36	

$$F = \frac{ssr}{sse} = \frac{0.51487}{0.00487} = 105.7$$

$$F_{0.01\ (3,33)} = 4.44$$

Therefore we reject H_1 $B_1 = B_2 = B_3 = 0$

TABLE XXX

ANALYSIS OF VARIANCE TABLE FOR TEST CASE II

Source	SS	d.f.	m.s.
SSR	1.50385	3	0.50128
SSE	0.20153	33	0.00611
SST	1.70538	36	

$F = 0.50128/0.00611 = 82.1$

$F_{0.01(3,33)} = 4.44$

Therefore we reject H; $B_1 = B_2 = B_4 = 0$

TABLE XXXI

ANALYSIS OF VARIANCE TABLE FOR TEST CASE V

Source	SS	d.f.	m.s.
SSR	1.92984	3	0.64328
SSE	0.35904	27	0.01330
SST	2.28888	30	

$F = 0.64328/0.01330 = 48.38$

$F_{0.01(3,27)} = 4.60$

Therefore we reject H; $B_1 = B_2 = B_3 = 0$

TABLE XXXII

ANALYSIS OF VARIANCE TABLE FOR TEST CASE VI

Source	SS	d.f.	m.s.
SSR	1.97319	3	0.65773
SSE	0.31568	27	0.01169
SST	2.28887	30	

$$F = 0.65773/0.01169 = 56.26$$

$$F_{0.01(3,27)} = 4.60$$

Therefore we reject H; $B_1 = B_2 = B_4 = 0$

TABLE XXXIII

ANALYSIS OF VARIANCE TABLE FOR TEST OF QUADRATIC TERMS FOR CASE III

Source	SS	d.f.	m.s.
SSR	1.65666	9	0.18407
SSE	0.04871	27	0.04871
SST	1.70537	36	

$$F = \frac{(1.65666 - 1.54463)}{6(0.04871)} = 0.383$$

$$F_{0.05(6,27)} = 2.46$$

Therefore we accept H;

$B_{11} = B_{12} = B_{13} = B_{22} = B_{23} = B_{33} = 0$

TABLE XXXIV

ANALYSIS OF VARIANCE TABLE FOR TEST OF QUADRATIC TERMS FOR CASE IV

Source	SS	d.f.	m.s.
SSR	1.66233	9	0.18470
SSE	0.04306	27	0.00159
SST	1.70539	36	

$$F = \frac{(1.66233 - 1.50385)}{6(.00159)} = 16.6$$

$$F_{0.01(6,27)} = 3.56$$

Therefore we reject H;

$$B_{11} = B_{12} = B_{14} = B_{22} = B_{24} = B_{44} = 0$$

TABLE XXXV

ANALYSIS OF VARIANCE TABLE FOR TEST OF QUADRATIC TERMS FOR CASE VII

Source	SS	d.f.	m.s.
SSR	2.23782	9	0.24865
SSE	0.05105	21	0.00243
SST	2.28887	30	

$$F = \frac{(2.23782 - 1.92984)}{6(0.00243)} = 21.1$$

$$F_{0.01(6,21)} = 3.81$$

Therefore we reject H;

$$B_{11} = B_{22} = B_{33} = B_{12} = B_{13} = B_{23} = 0$$

TABLE XXXVI

ANALYSIS OF VARIANCE TABLE FOR TEST OF QUADRATIC TERMS FOR CASE VIII

Source	SS	d.f.	m.s.
SSR	2.218251	9	0.246472
SSE	0.070624	21	0.003363
SST	2.288875	30	

$$F = \frac{(2.218251 - 1.973195)}{6(0.003363)} = 12.15$$

$$F_{0.01(6,21)} = 3.81$$

Therefore we reject H;

$$B_{11} = B_{12} = B_{14} = B_{22} = B_{24} = B_{44} = 0$$

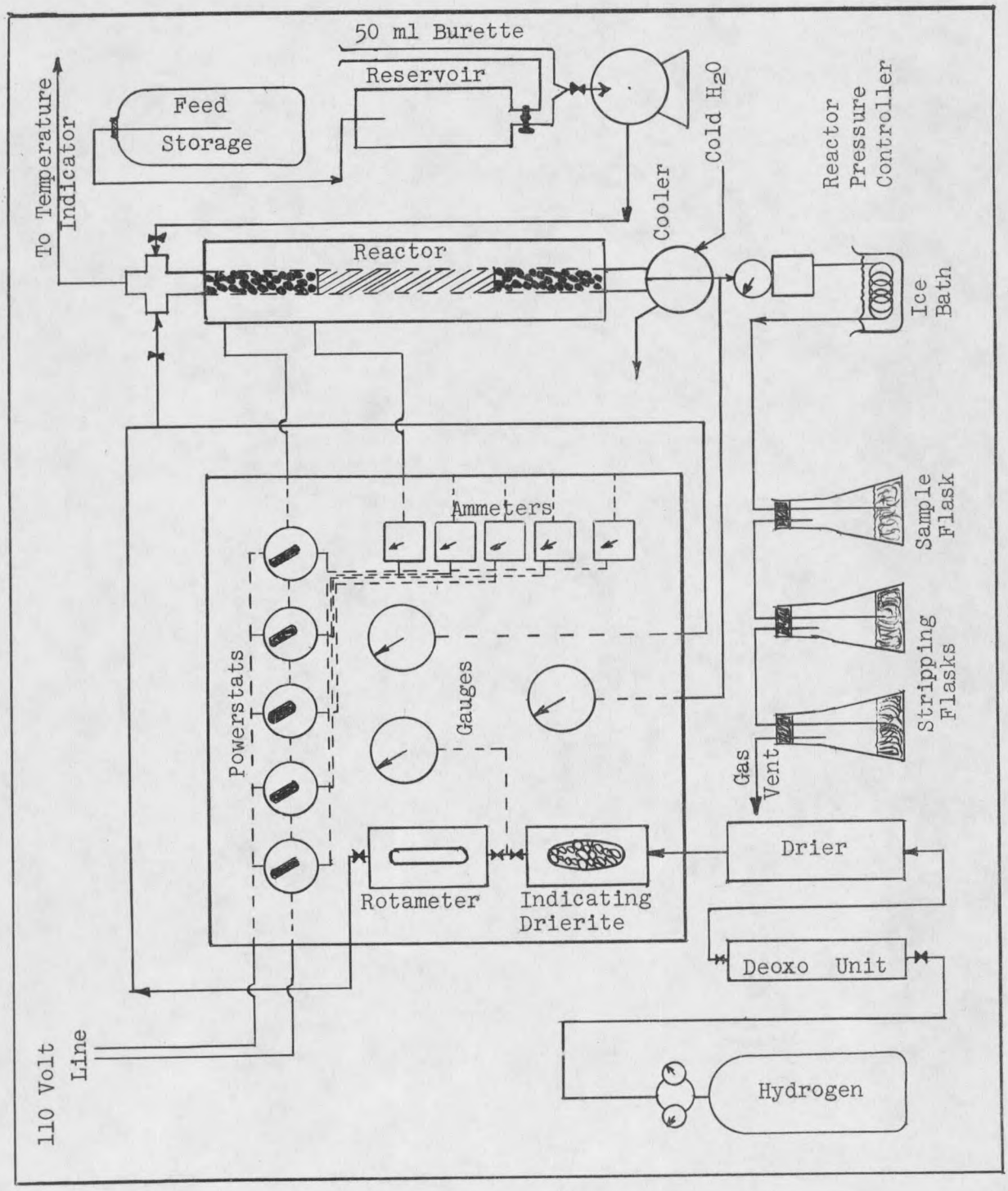

Figure 1. Schematic Flow Diagram of Hydrogenation Unit

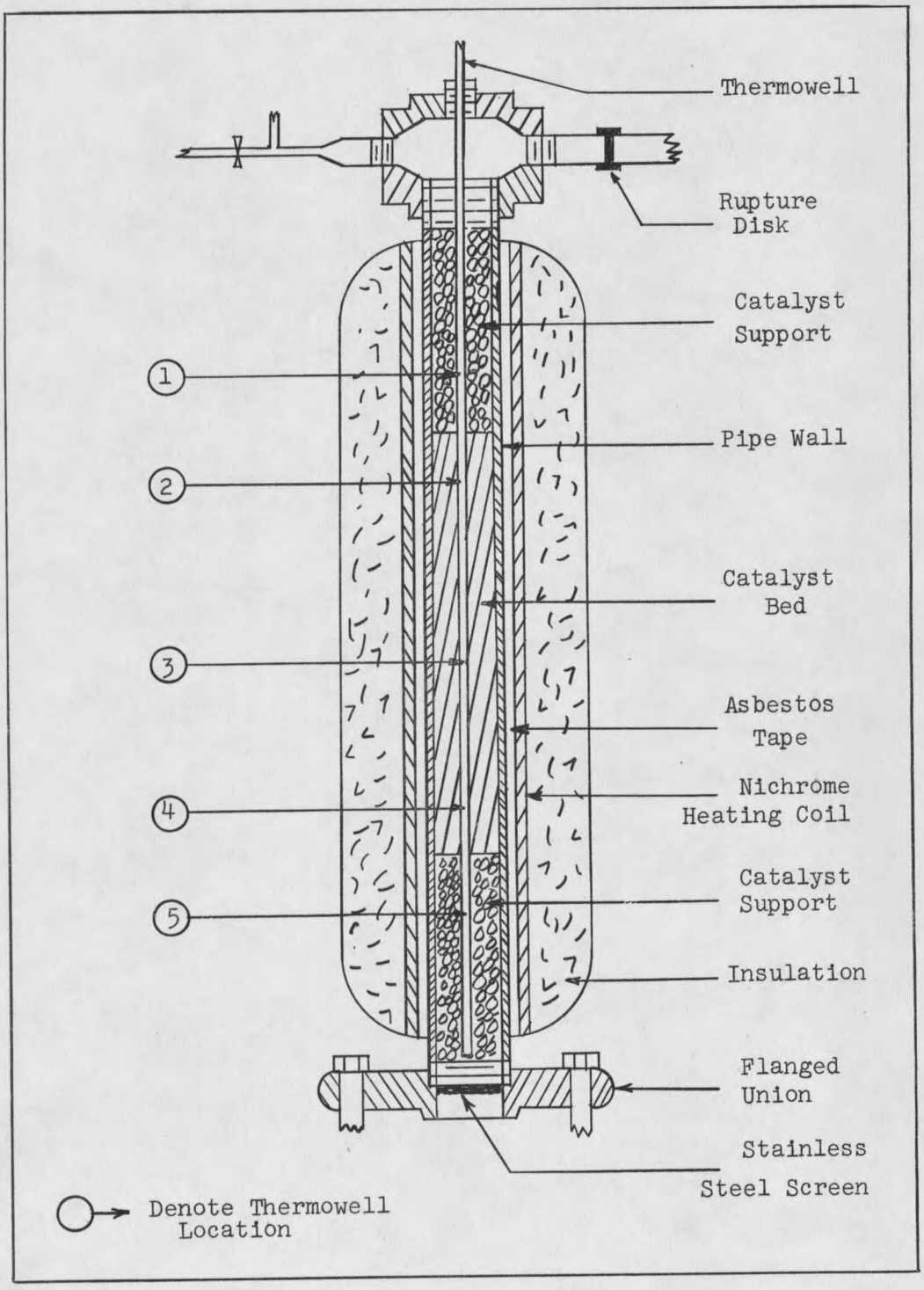

Figure 2. Detailed Diagram of Reactor

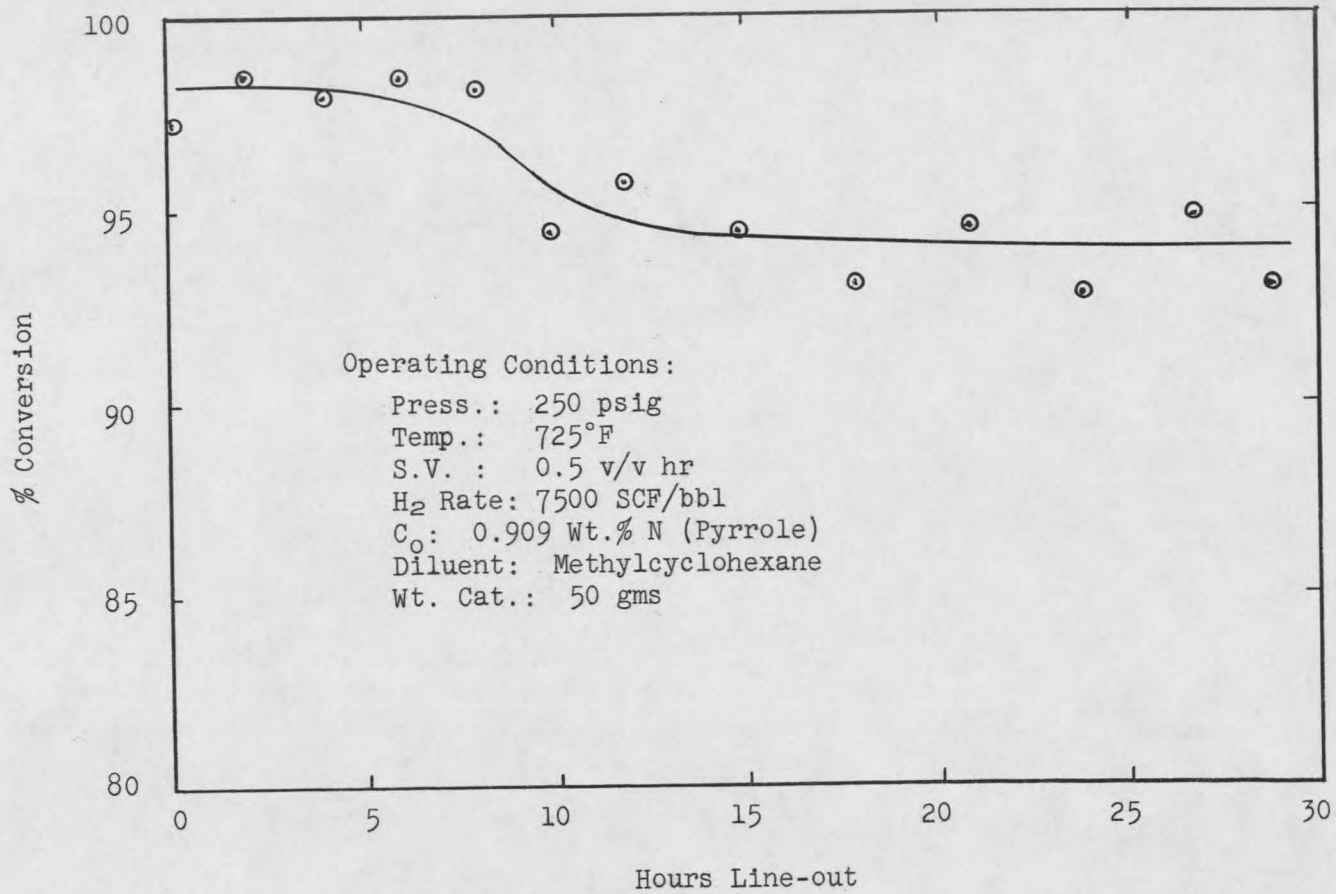

Figure 3. Conversion vs. Hours after Line-out to Determine Length of Time Before Sampling

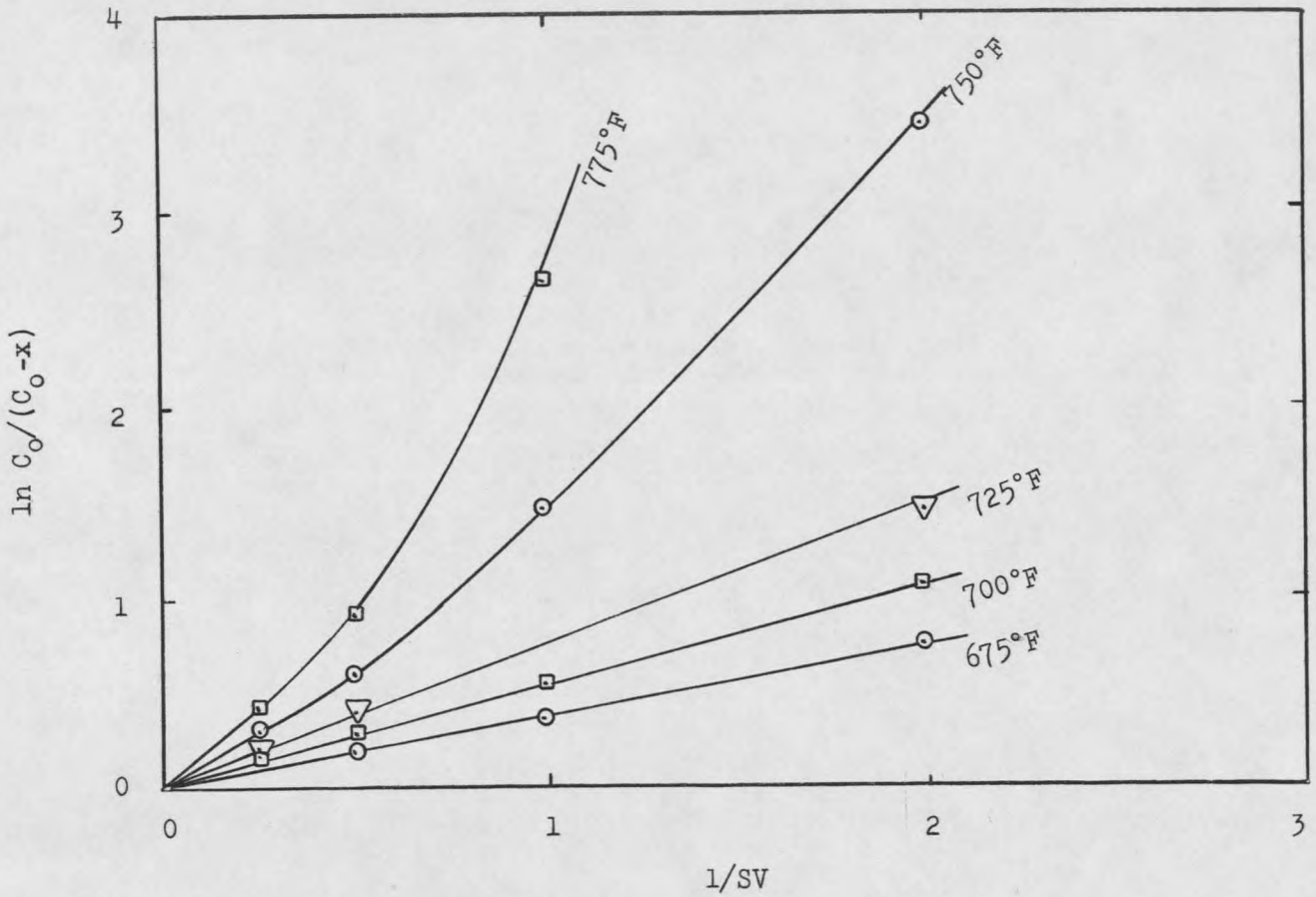

Figure 4. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Toluene (C_o = 1).

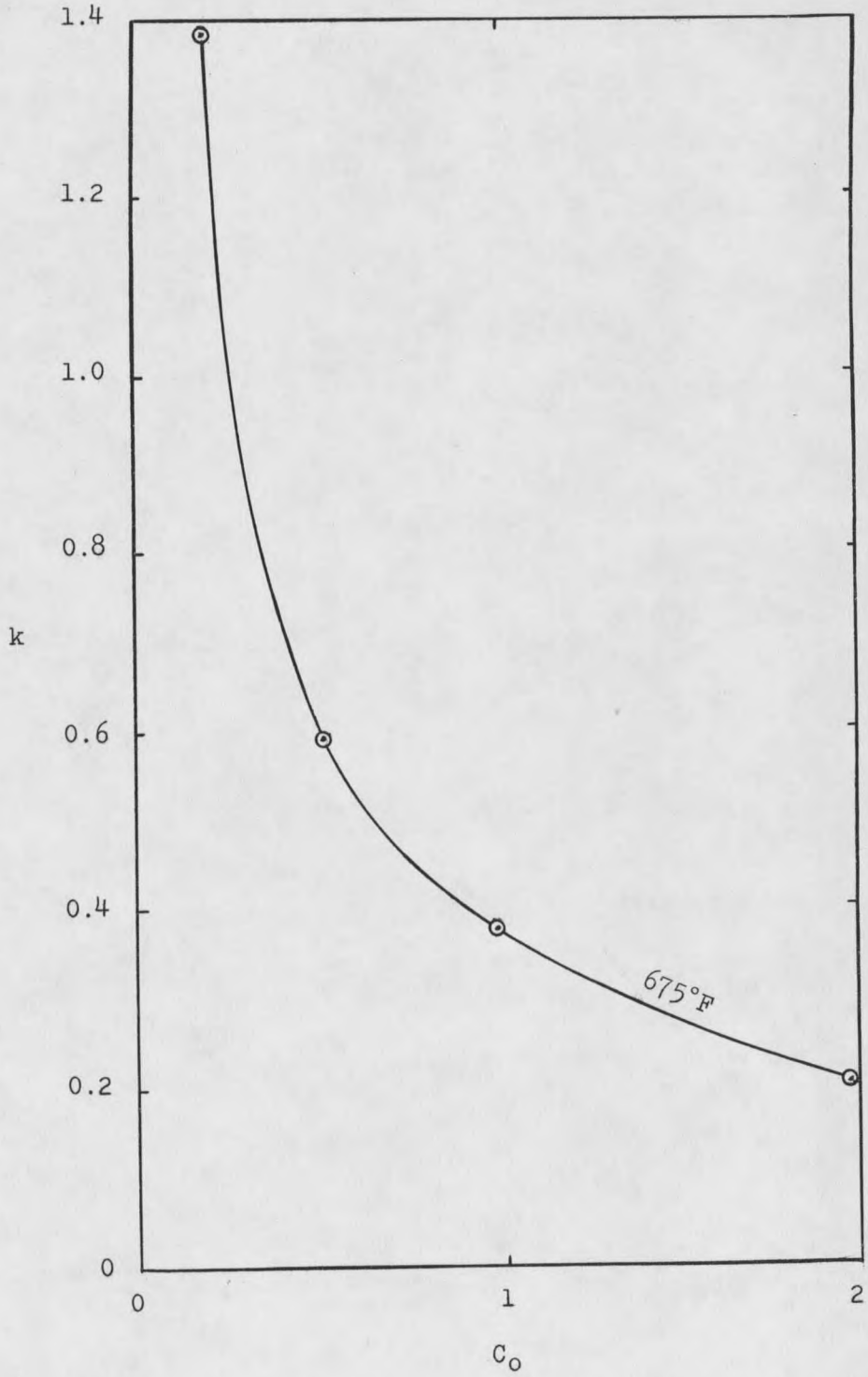

Figure 5. Reaction Rate Constant vs. Initial Concentration for Pyridine in Toluene

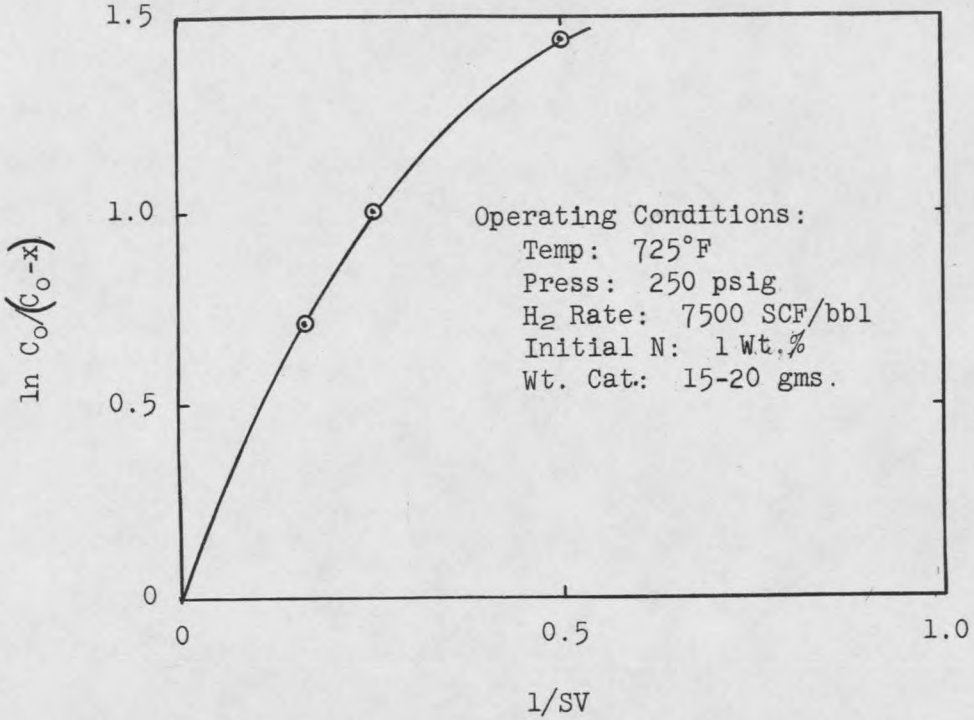

Figure 6. Plot of ln $C_o/(C_o-x)$ vs Reciprocal Space Velocity for Pyrrole in Toluene

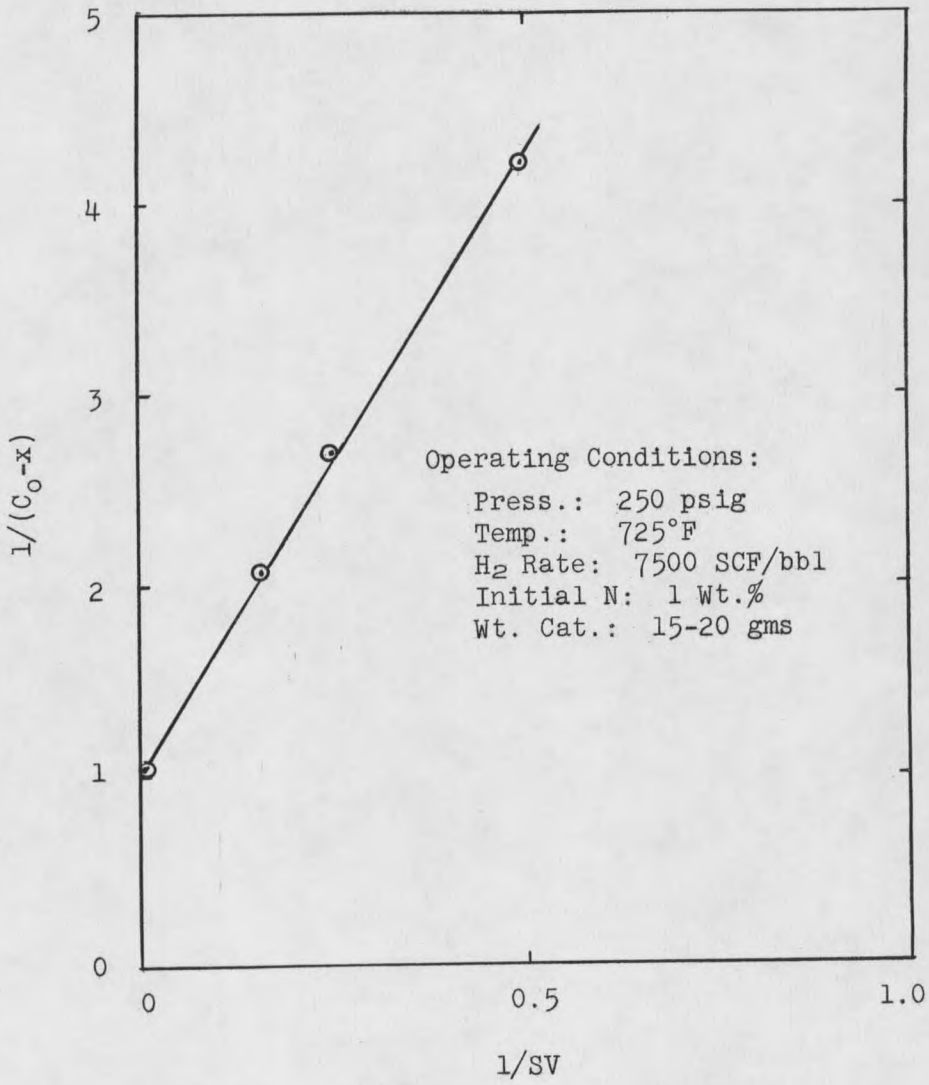

Figure 7. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

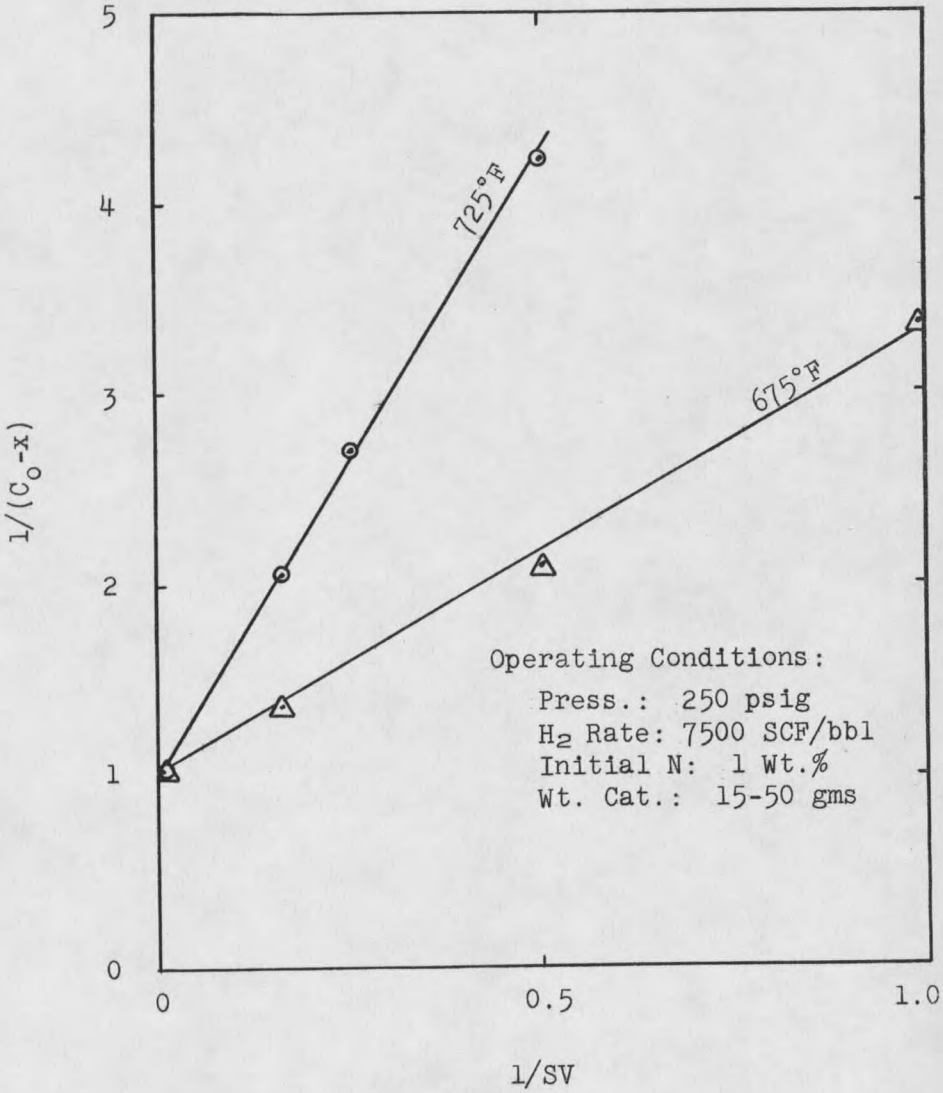

Figure 8. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

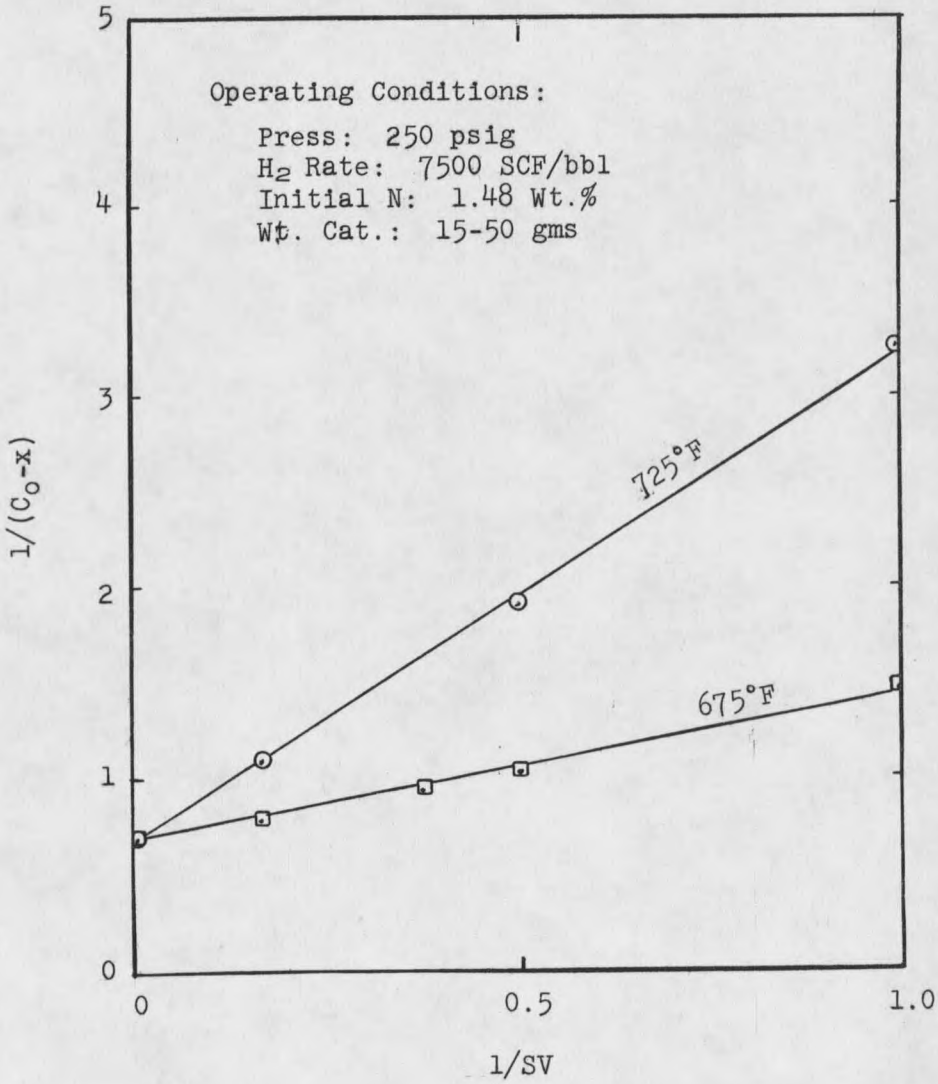

Figure 9. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

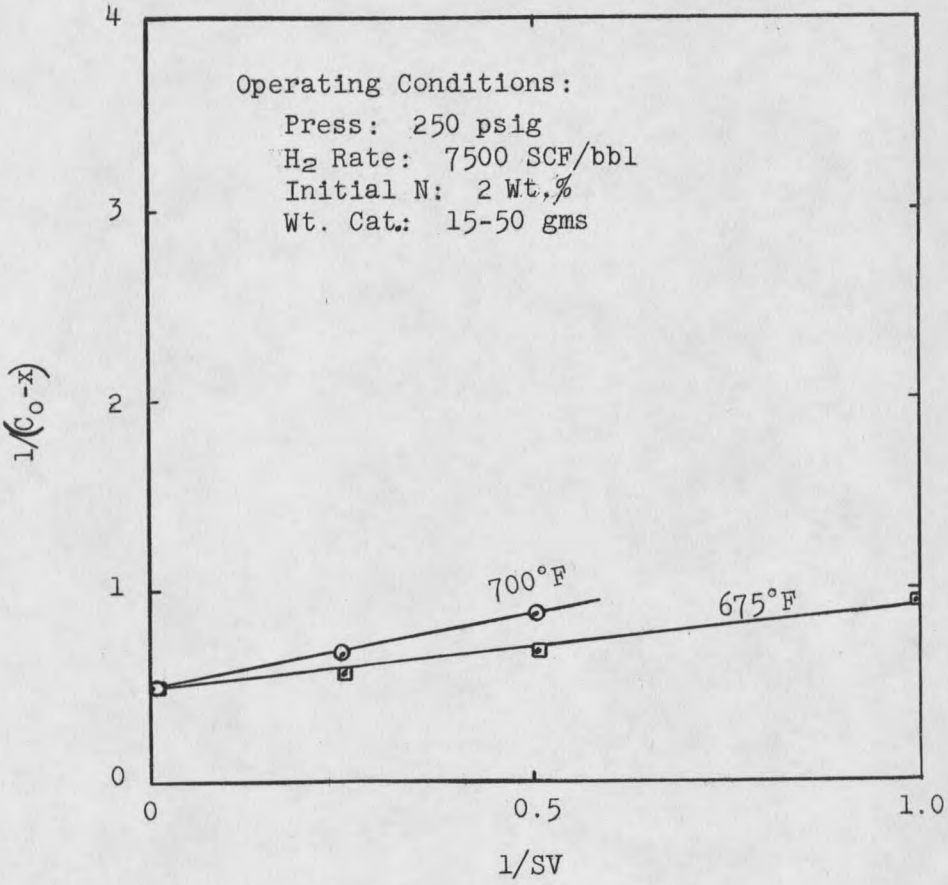

Figure 10. Plot of $1/(C_o-x)$ vs Reciprocal Space Velocity for Pyrrole in Toluene.

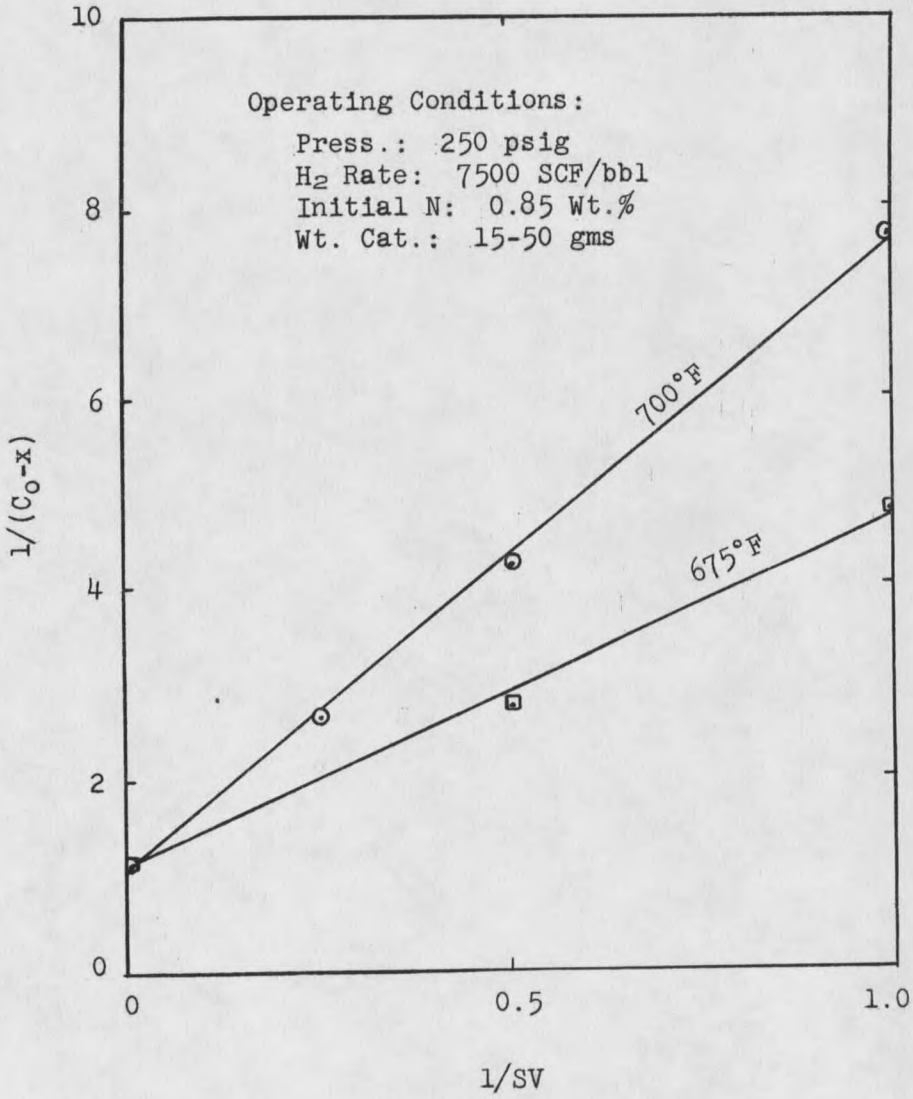

Figure 11. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

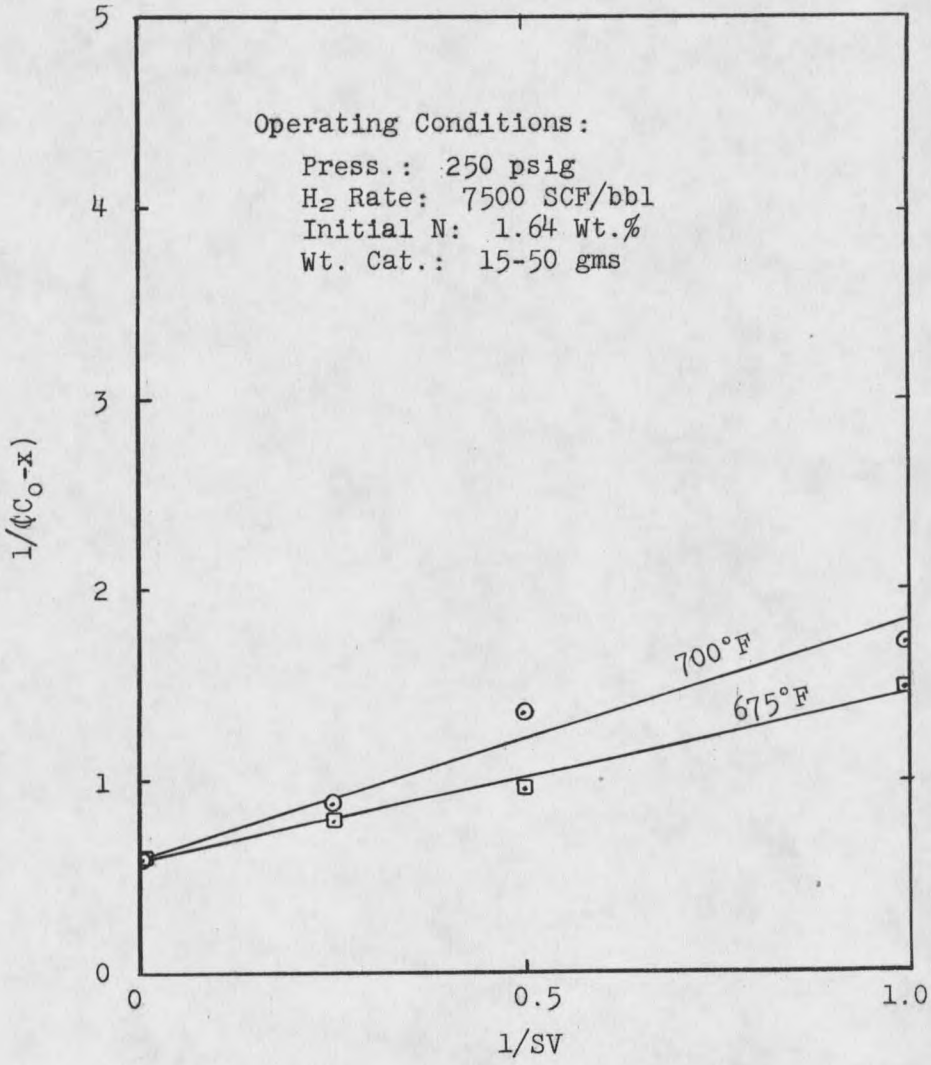

Figure 12. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

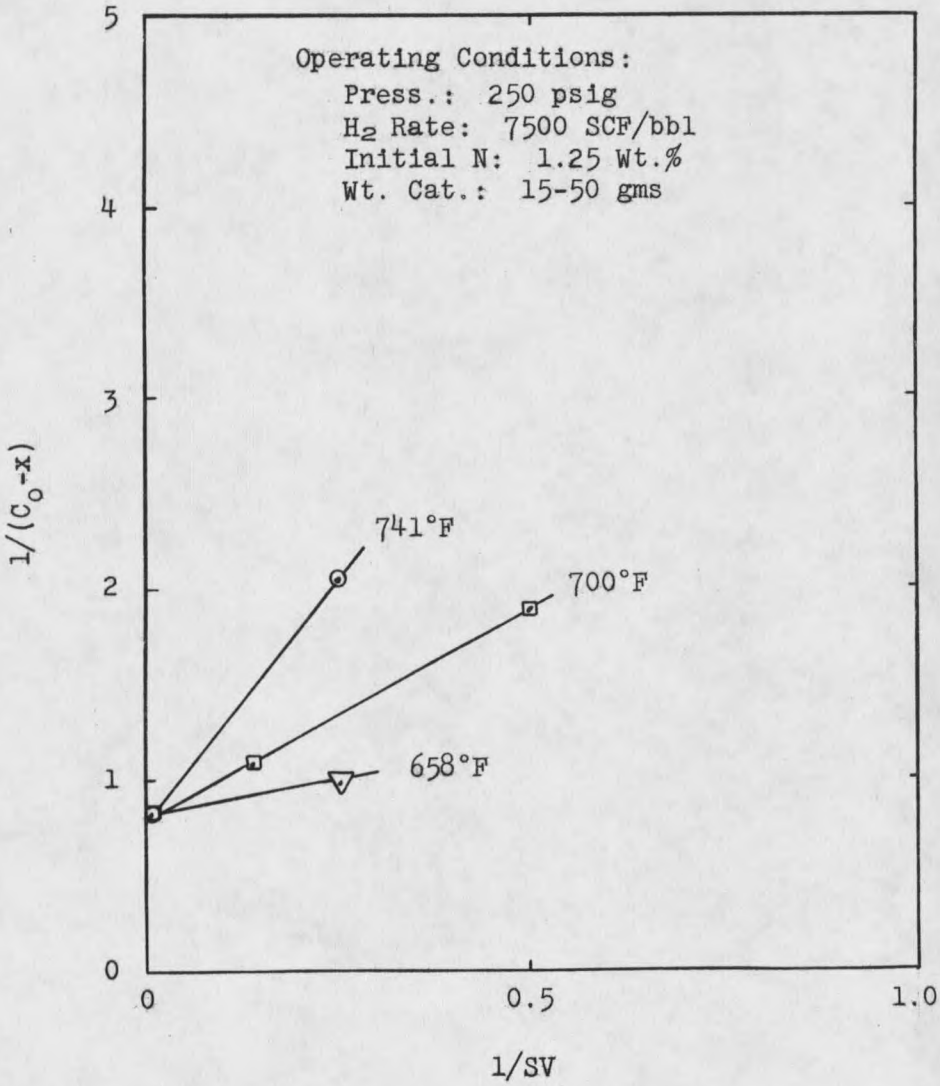

Figure 13. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene

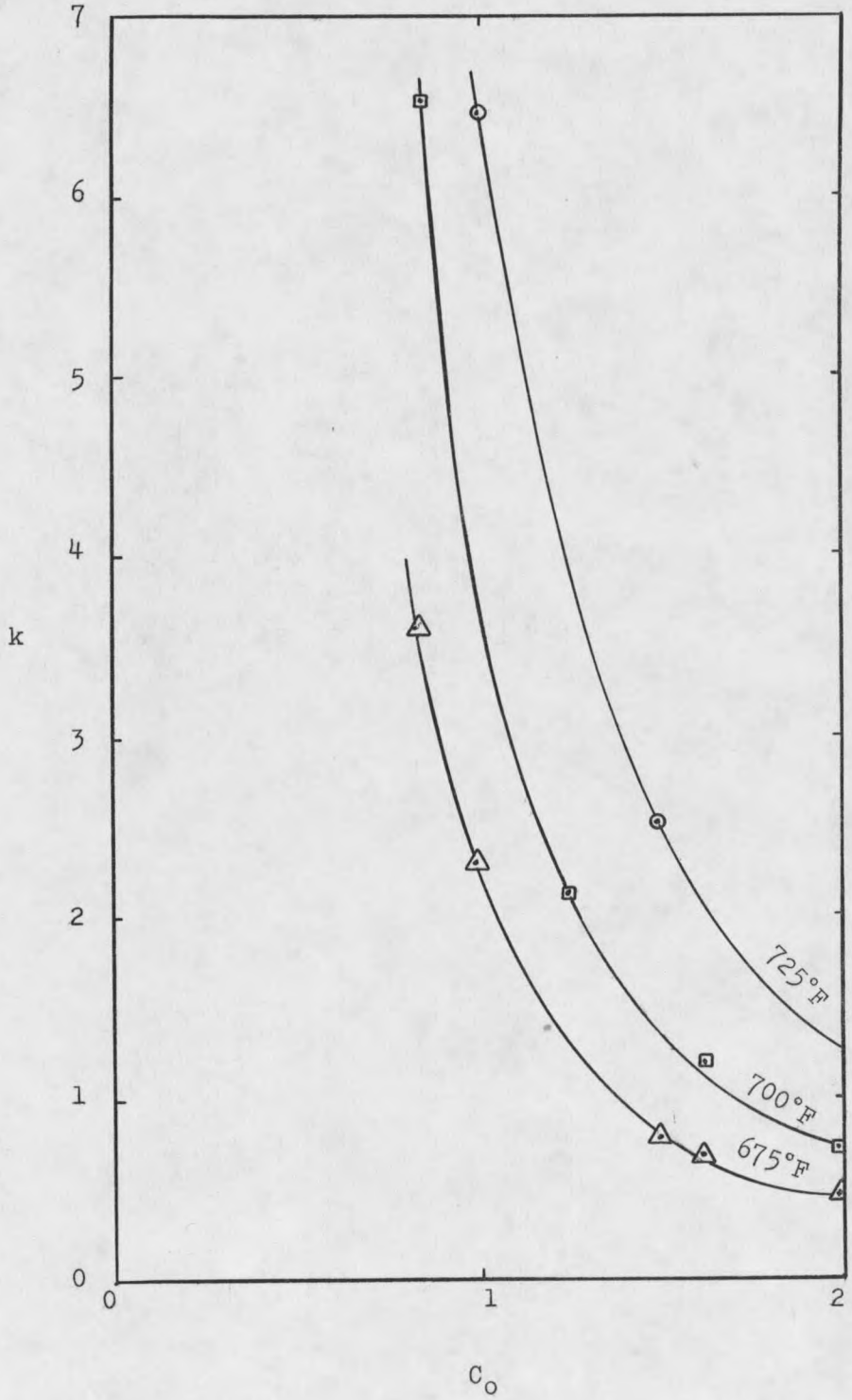

Figure 14. Reaction Rate Constant vs. Initial Concentration for Pyrrole in Toluene

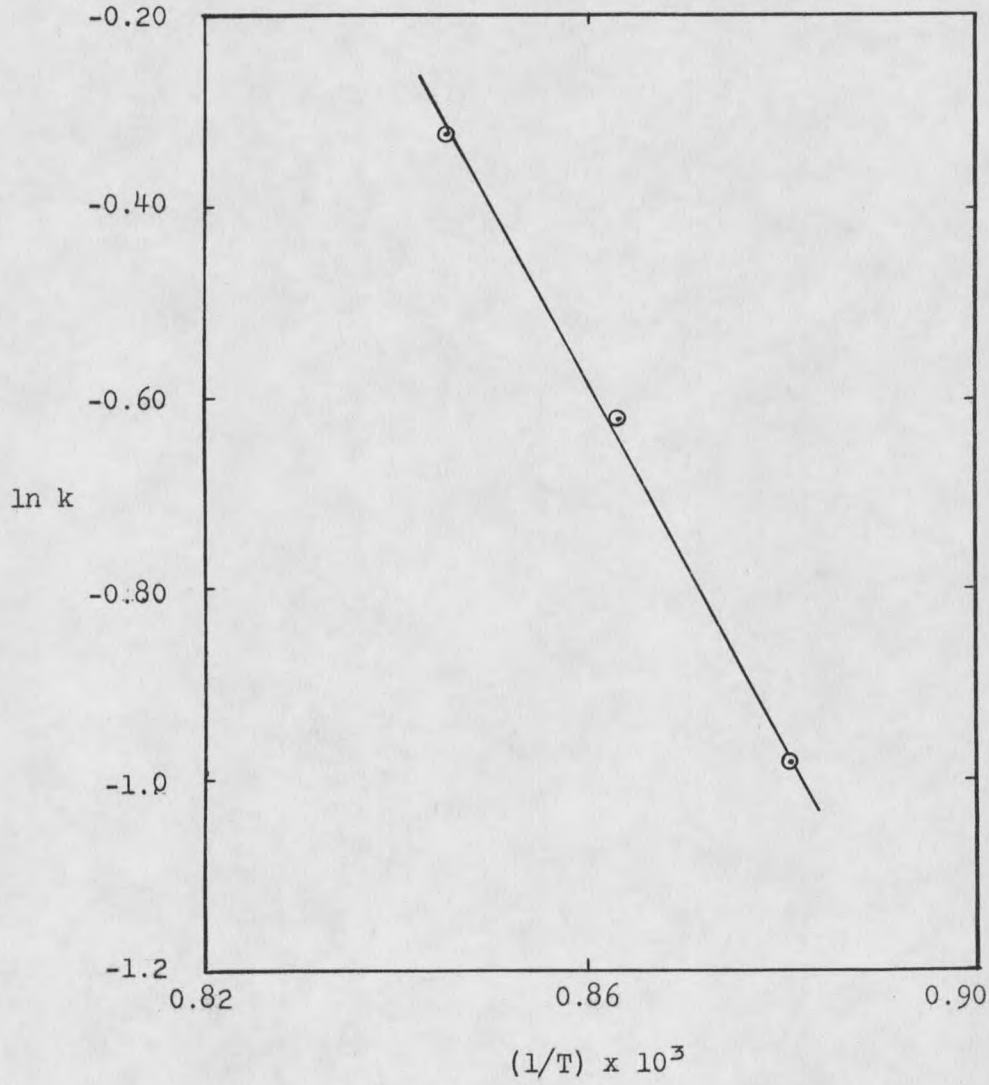

Figure 15. Plot of ln k vs. 1/T for Pyridine in Toluene

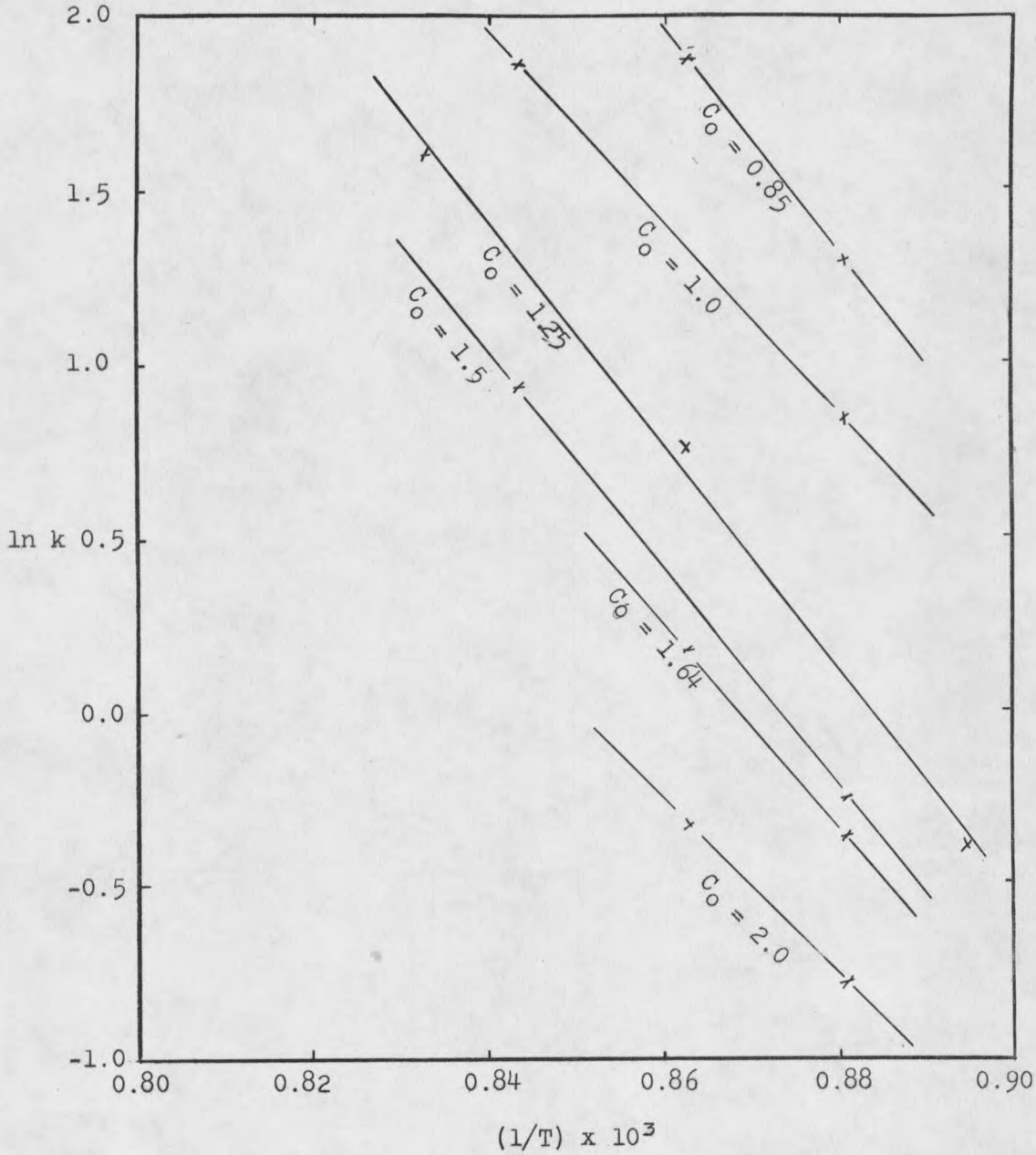

Figure 16. Plot of ln k vs. 1/T for Pyrrole in Toluene

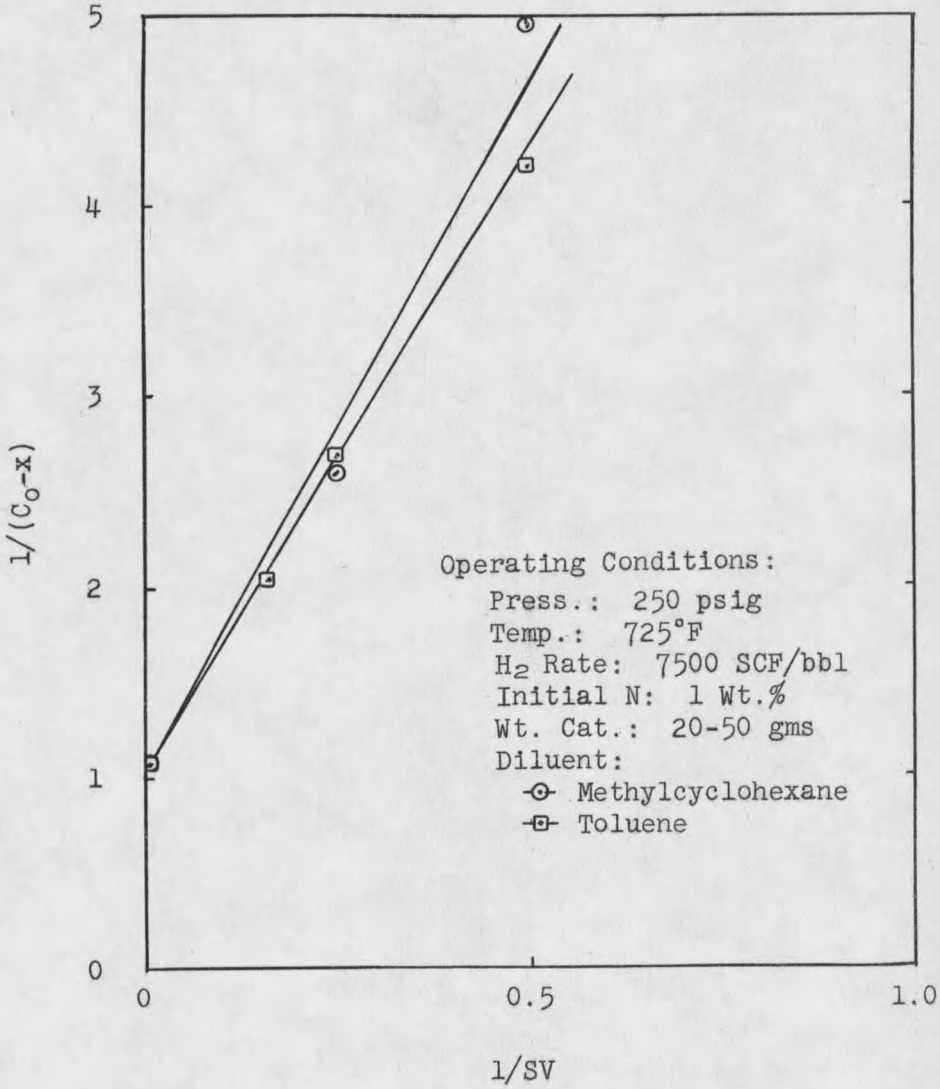

Figure 17. Plot of $1/(C_o-x)$ vs. Reciprocal Space Velocity for Pyrrole in Toluene and Methylcyclohexane

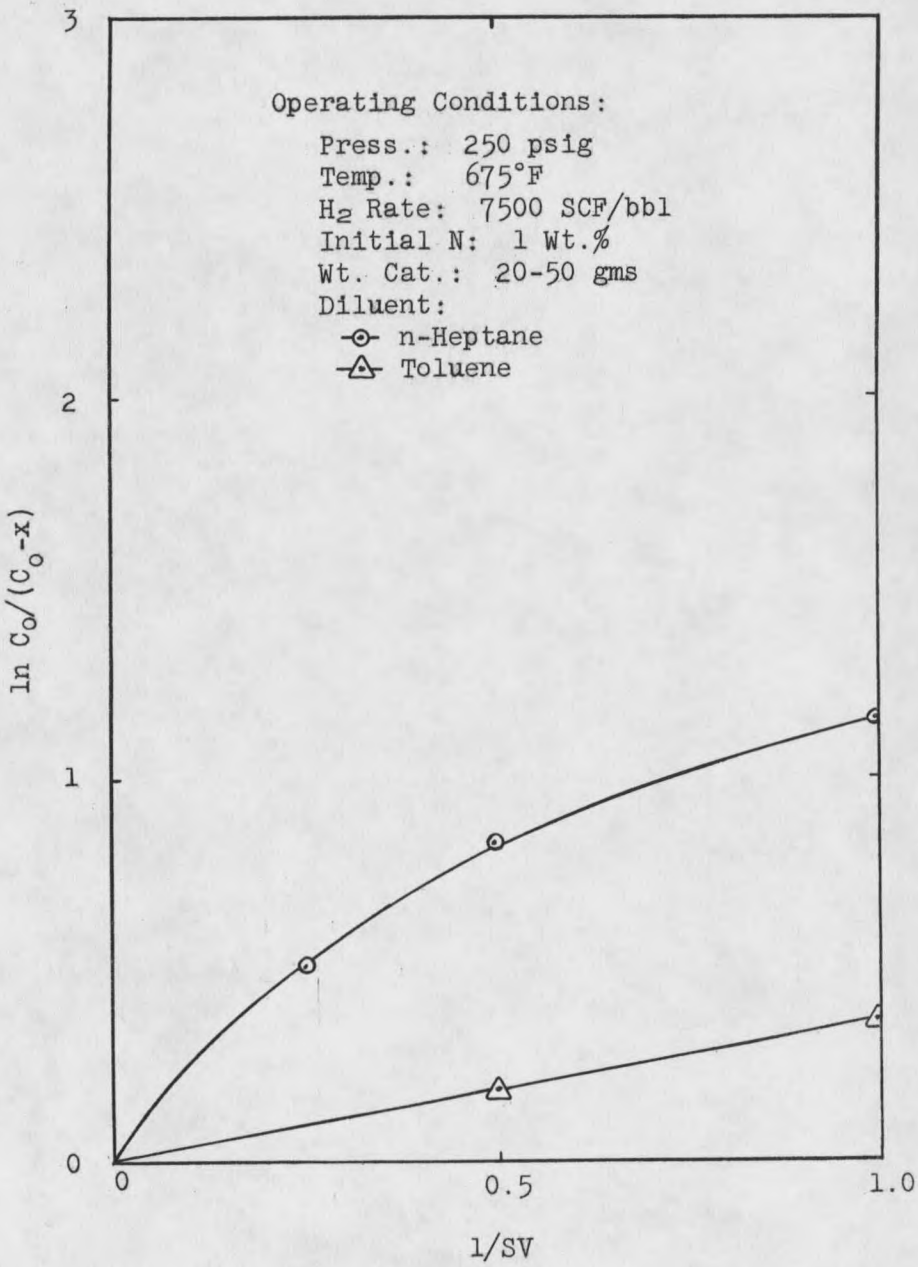

Figure 18. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Toluene and n-Heptane

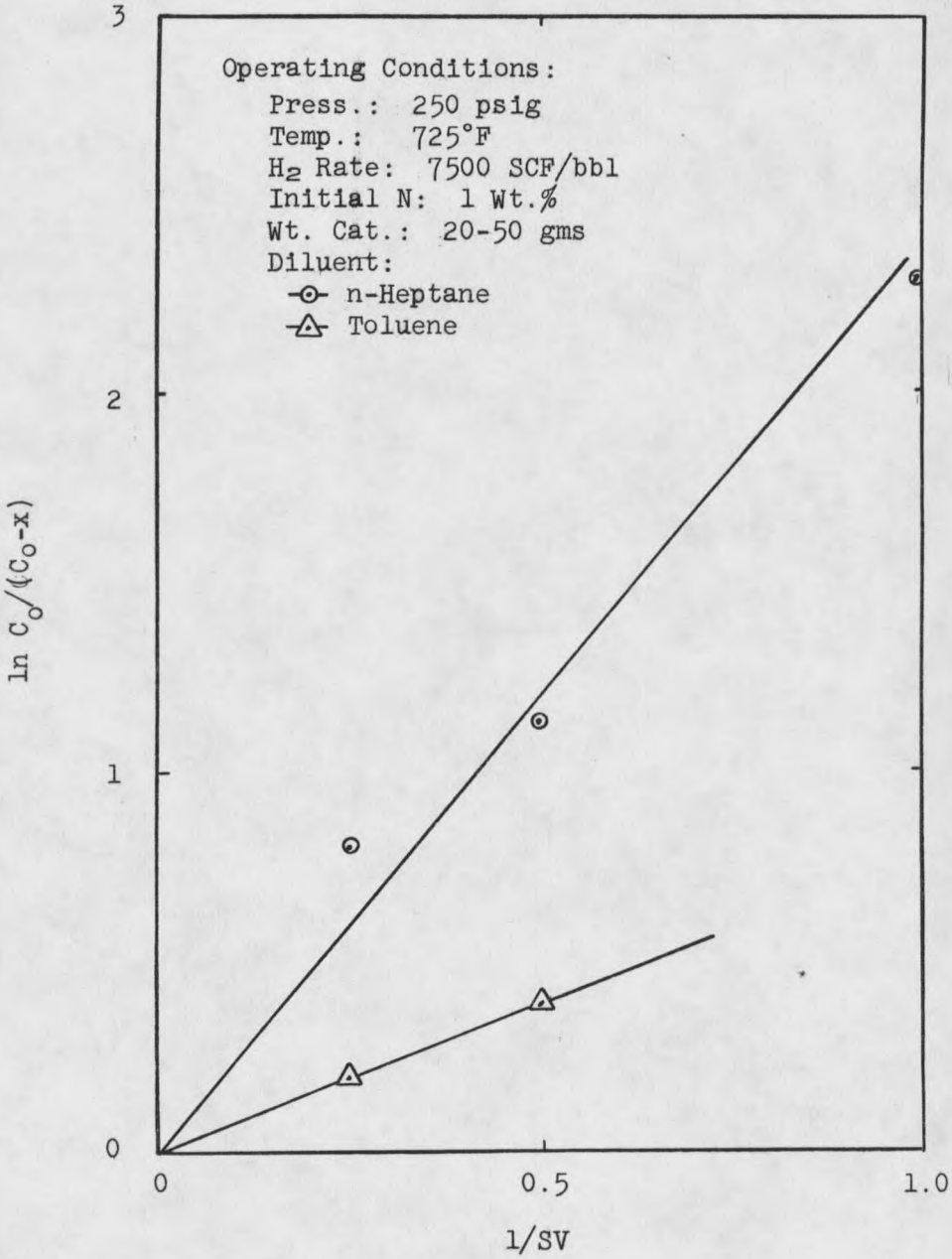

Figure 19. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Toluene and n-Heptane

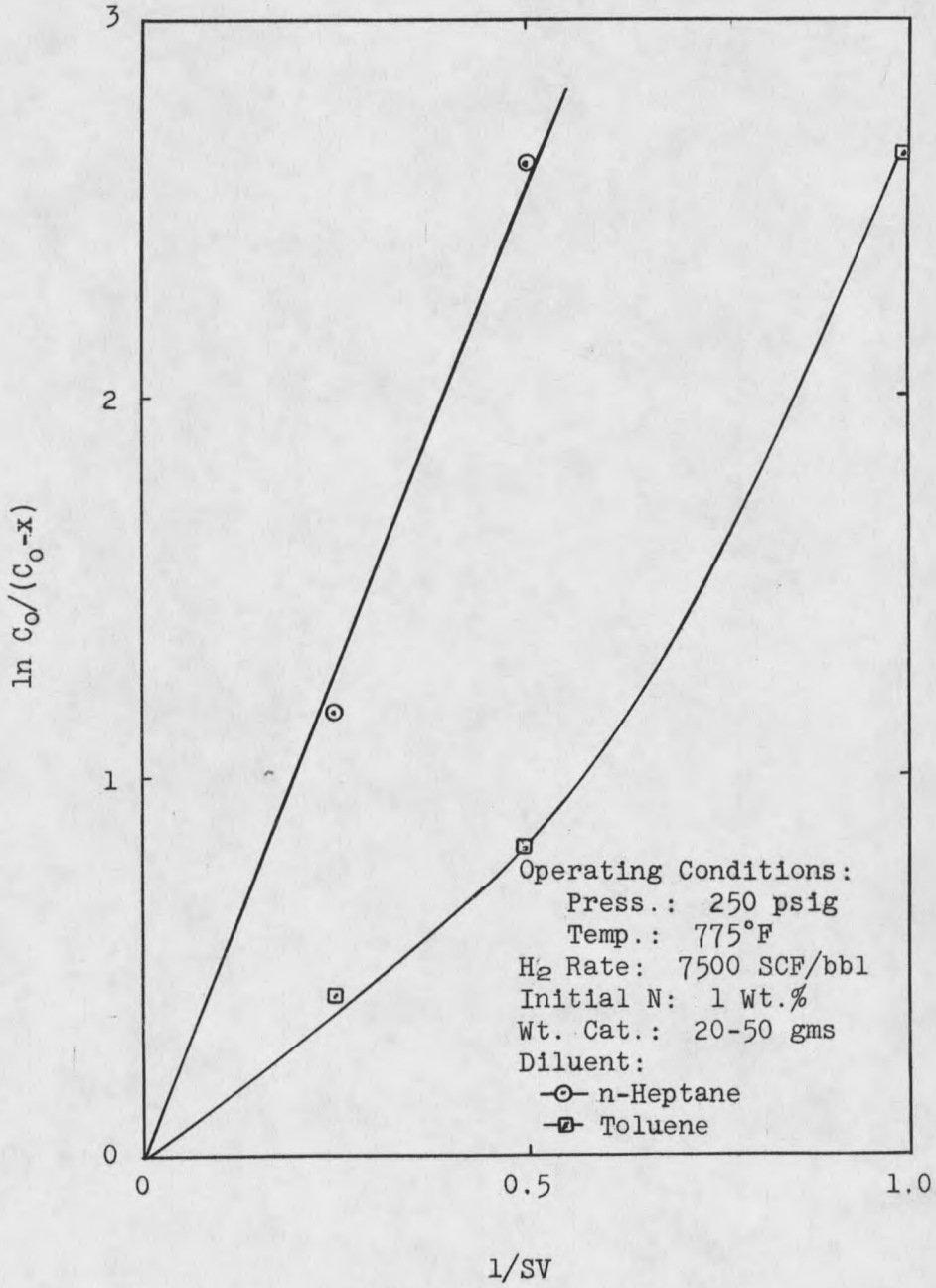

Figure 20. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Toluene and n-Heptane

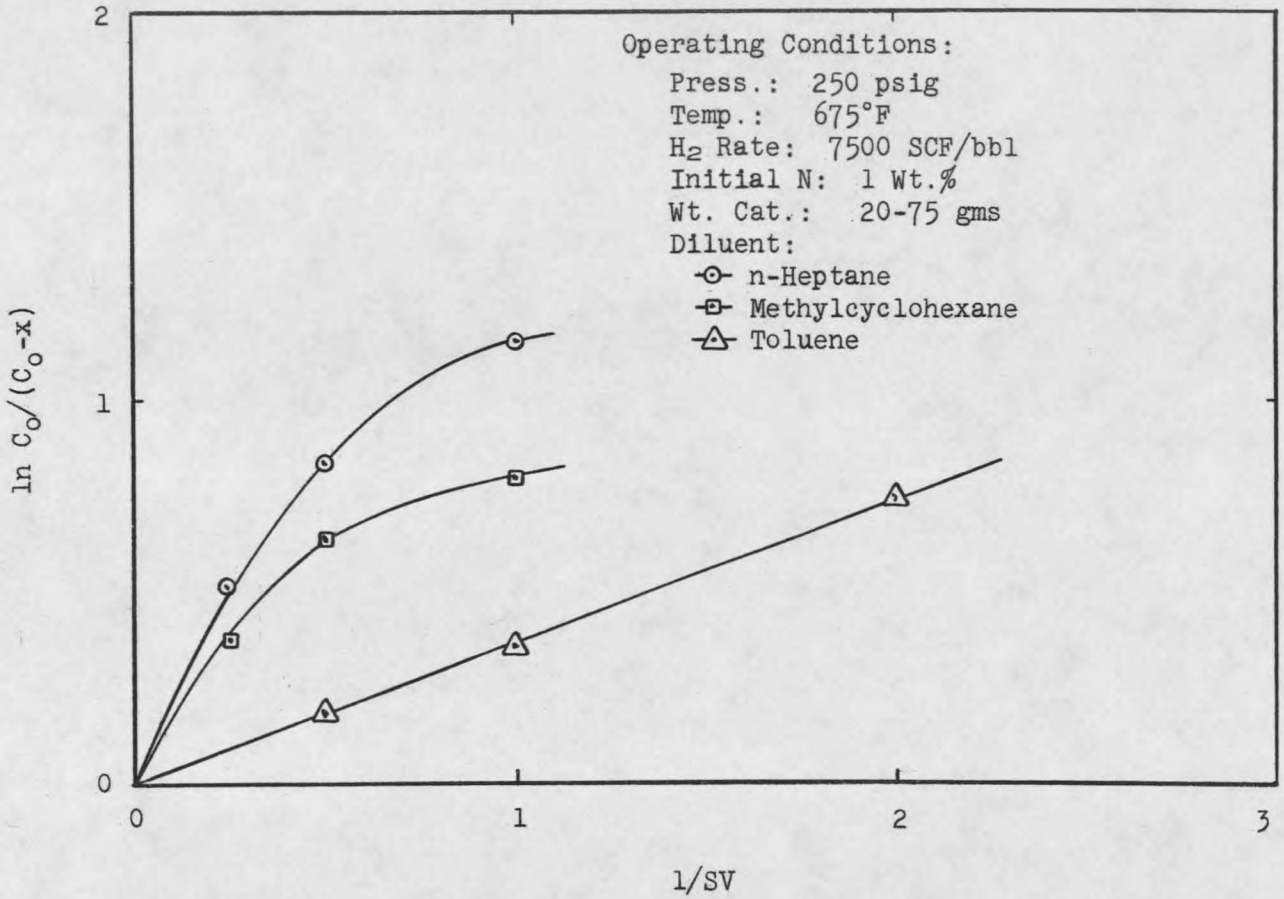

Figure 21. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Toluene, n-Heptane, and Methylcyclohexane

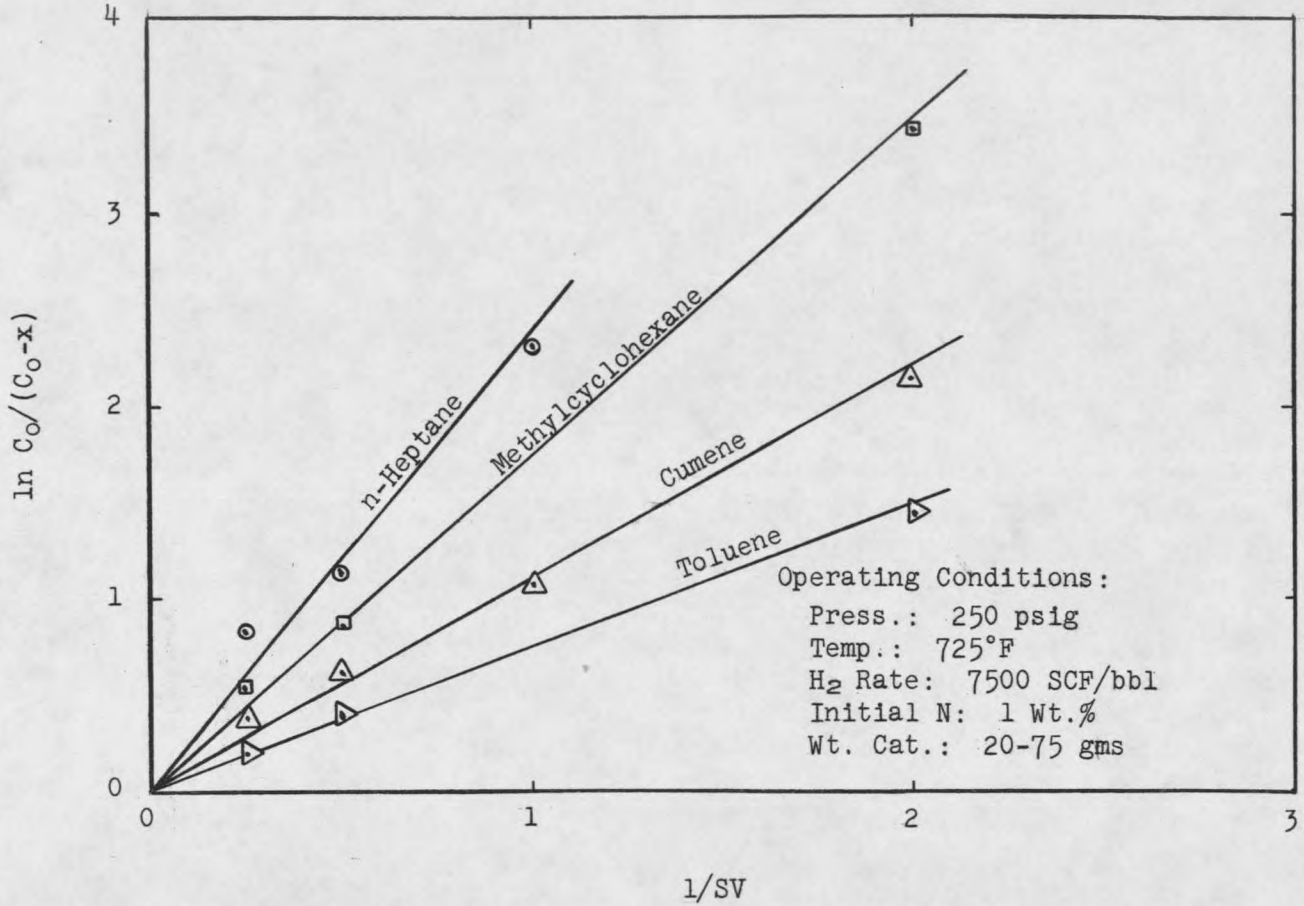

Figure 22. Plot of ln $C_o/(C_o-x)$ vs. Reciprocal Space Velocity for Pyridine in Various Diluents

CURRICULUM VITA

Gary Paul Schreiber

PERSONAL

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EDUCATIONAL

High School: Billings Senior High School, Billings, Montana; 9/50 to 6/54

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EXPERIENCE

Summer employee with the E. I. du Pont de Nemours & Company, Paints and Varnishes Plant, Chicago, Illinois; 6/57 to 9/57

Research Fellow in Chemical Engineering, Montana State College, Bozeman, Montana; 6/58 to Date

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