

PSEUDO REACTION KINETICS
AND
HYDROCRACKING
OF
2,6-LUTIDINE

by

Karl A. McKinstry

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

Signed: Karl A. McKinstry
Karl A. McKinstry

Golden, Colorado

Date: October 10, 1968

Approved: James H. Gary
Dr. James H. Gary
Thesis Advisor

James H. Gary
Dr. James H. Gary
Head, Chemical and
Petroleum Refining
Engineering Department

Golden, Colorado

Date: October 10, 1968

DEDICATION

To my parents,
whose years of encouragement
have made this study possible

ABSTRACT

The purpose of this research was to study the reaction of 2,6-lutidine in a hydrocracking environment with a nickel tungsten catalyst. The reaction was studied in a high-pressure batch reactor where the reaction conditions of temperature, pressure, and reaction times varied from 400°F to 750°F, 400 psig to 750 psig, and 2 to 6 hours. The main objective of this study was to determine the order of the reaction of disappearance of 2,6-lutidine. The pseudo order, reaction rate constants, and the activation energy were determined. Several replicate runs were made to determine the variance of the experimental runs.

The reaction of 2,6-lutidine at temperatures and pressures above 600 F and 600 psig produces many products, which were classified in groups as C₃, C₄, C₅, C₆, C₇, C₈, and basic amines. At temperatures of 750°F and pressures above 600 psig, the conversion of 2,6-lutidine produced over 70-weight percent hydrocarbons.

An empirical equation based on the Arrhenius dependency was determined to calculate the reaction rate constants from the activation energy in the temperature range of 400°F to

750°F. The variance of the experimental data was described by a model where a mean expected profit and a variability of this profit was determined if the product was sold at a profit of \$1 per weight percent of sample. The range was determined to be $\$100 \pm \12.68 at a probability of 0.70 for the maximum range of the replicate runs studied.

ACKNOWLEDGMENTS

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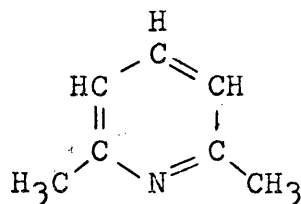
INTRODUCTION

Shale oil has been a controversial subject for the past ten years in the United States. Many individuals have questioned the feasibility of using this abundant natural resource to supplement our country's petroleum needs. In particular, the development of shale oil will effect the future economy of Colorado, Utah, and Wyoming. Many technical studies have been made to try to understand the nature and the processing of shale oil to usable petroleum products, but much of this information is still unpublished.

The high percentage of sulfur and nitrogen in shale oil has created a possible problem in the processing of shale oil not usually associated with petroleum crude. These percentages are much higher than for crude petroleum. A sensible way to process the shale oil to usable petroleum derivatives would be hydrotreating or hydrocracking. Naphthas from Colorado shale oil contain about 1-percent nitrogen, which corresponds to about 10-percent nitrogen-containing compounds (1).

The particular objective of this thesis is to determine the kinetics of 2,6-lutidine (2,6-Dimethylpyridine) reactions in a catalytic hydrocracking environment. This compound has

been indentified in shale oil and shale oil naphtha, and was selected because a large amount of this nitrogen compound is found in shale oil. The estimated amount found in naphtha is 0.01 volume percent (2). A homologue of pyridine, 2,6-lutidine has the following structure:

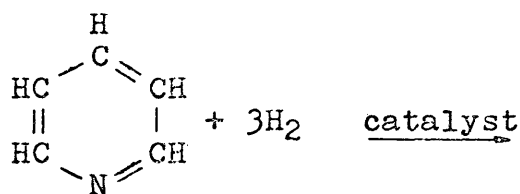


there are many other nitrogen-containing compounds that could be studied in a similar manner.

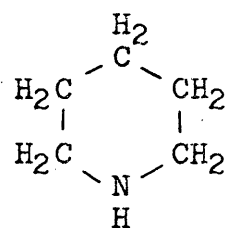
This thesis entails the following structure: The previous work in this area is discussed. The experimental equipment and the design of the experiment are explained in detail. Next, the experimental procedure and method of sample analysis is discussed. The results which include system analysis, conversion of 2,6-lutidine to products, determination of the pseudo kinetics, the activation energy and experimental error are discussed.

LITERATURE SURVEY

The catalytic hydrogenation of the pyridinoid nucleus has been carried out under various conditions by many investigators. With most catalysts and temperatures below 250 to 300°C, the hydrogenation of the pyridinoid nucleus is (3)



pyridine



piperidine

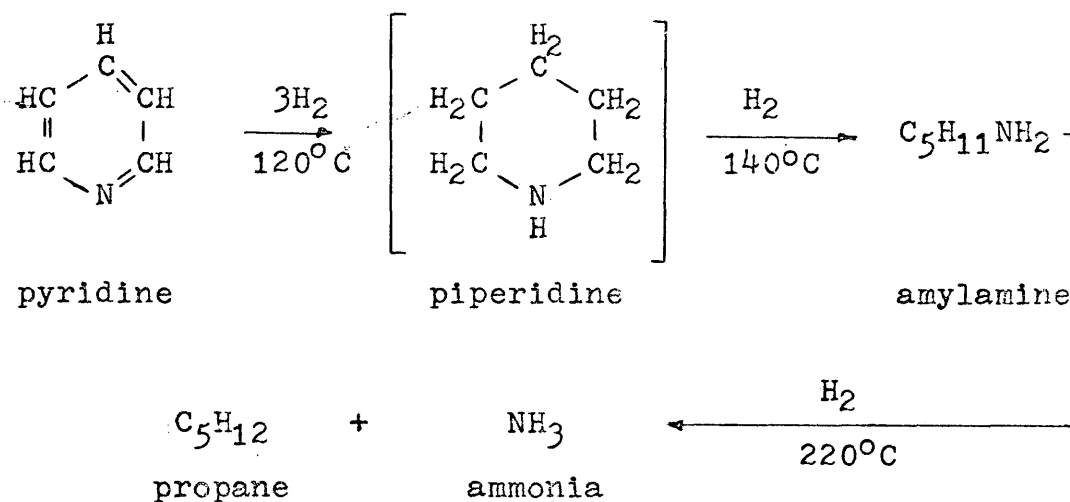
As early as 1912 Skita and Meyer (4) successfully reduced pyridine at low temperature over colloidal platinum as a catalyst. Other catalysts used for the hydrogenation of the pyridinoid nucleus include nickel on kieselguhr, Raney nickel, copper-chromite, and palladium on asbestos. The high temperatures and pressures necessary for successful conversion of pyridine and its derivatives also favor side reactions.

Adkins (5) investigated the occurrence of side reactions and concluded temperature control was an important factor in the hydrogenation of the pyridinoid ring with nickel catalysts.

The main side reactions consisted of three types:

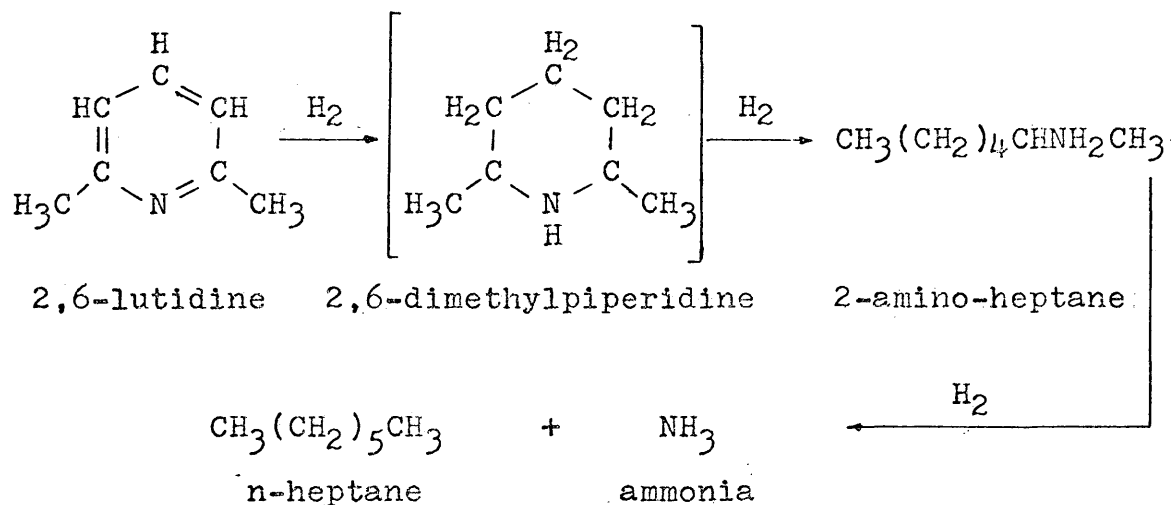
1. Rupture of the carbon-nitrogen bond,
2. Alkylation of the secondary amine formed by hydrogenation,
3. Condensation of various intermediate products.

Rupture of the carbon-nitrogen bond is probably an effect of the temperature and catalyst. Sabatier (6) reported the production of amylamine when pyridine and hydrogen gas is passed over nickel. Pyridine is slowly attacked by hydrogen gas over nickel between 120 to 220°C, opening the ring to form amylamine. It is proposed that decomposition or cracking occurs as the temperature increases (7).



This reaction supposes that cracking and hydrogenation of the pyridinoid nucleus is possible with a suitable catalyst and appropriate temperature and pressure. A saturated hydrocarbon is produced with the release of ammonia gas. Likewise, it could be postulated that 2,6-lutidine behaves

in a similar manner according to the equation:



This is the basis of this study, the production of a measurable quantity of a saturated hydrocarbon to determine kinetics.

Adkins and co-workers (8) investigated the hydrogenation of substituted pyridines at elevated temperatures and pressures. It was noted that less severe conditions are necessary to hydrogenate derivatives of pyridine with substitutes on the 2 or 2,6 positions.

Smith and Stanfield (9) studied the hydrogenation of methyl pyridines over Adams platinum catalyst in acetic acid as a solvent, with hydrogen pressures of 16 to 64 psia and temperatures of 15 to 45°C. The products were methylpiperidines.

It has been postulated that the hydrogenation of the ring, rupture of the carbon-nitrogen bond, and stripping of the nitrogen from the chain is possible for methylpyridines,

but no detailed investigation of this conversion has been made.

The conversion of hydrocarbons to compounds of lower molecular weight in the presence of hydrogen, over an acidic catalyst containing a hydrogenating component is described as hydrocracking. Other pseudo names that can describe the cracking are hydrotreating or denitrogenation.

Several other reactions can occur if conditions such as pressure and temperature are suitable. These are isomerization, hydrogen transfer, and hydrogenation. Reactions are carried out at temperatures of 400 to 800°F and pressures of 400 to 1000 psia (10). Since this investigation is directly related to the hydrotreating of shale oil stocks, the above temperatures and pressures are in the range that previous shale oil hydrotreating work has been done. The mechanism of hydrocracking follows the carbonium ion mechanism of catalytic cracking with hydrogenation superimposed. Several hydrogenation catalysts mentioned previously have been used; but a hydrocracking, hydrotreating or in particular a denitrogenation catalyst must be used to accomplish the objective on nitrogen removal and hydrogenation of the unsaturated carbons.

The removal of nitrogen compounds industrially is usually accomplished by hydrogenation over cobalt-molybdate or nickel-tungsten-sulfide catalysts. The nickel-tungsten-sulfide catalyst, in general, produces the following effects in

the cracking of hydrocarbons, especially paraffinic or olefinic materials (11):

1. No isomerization of charge,
2. Cyclic formation small or not noted,
3. Secondary splitting extensive, mainly to $C_3 - C_7$.

DESCRIPTION OF EQUIPMENT

The experimental equipment consisted of a high-pressure reactor manufactured by Parr Instrument Company. The reactor apparatus is listed under Series 4511 Pressure Reaction Apparatus in the Parr Catalog. The bench-scale reactor had additional modifications to make it suitable for the experimental study. Figure 1 shows the experimental apparatus. The reactor is built for chemical reactions, liquid or gaseous, requiring temperatures and pressures up to 400°C (752°F) and 1000 psig (68 atm). The bomb's thermowell and electrical heating system were modified. In place of the thermowell, a thermocouple was used to obtain a much more sensitive temperature reading within the reactor. The electrical heating system was not sufficient to maintain the high temperature.

The standard pressure reaction apparatus contains a 1500-watt heater; an additional heater, rated at 500 watts, was placed at the base of the reaction bomb. The additional heater served a two-fold purpose: to increase the temperature faster at start up and to help maintain the required temperature at the high-temperature runs because the output of the original heater was not sufficient. The heaters were manually regulated by two 110-volt Powerstats. The thermowell

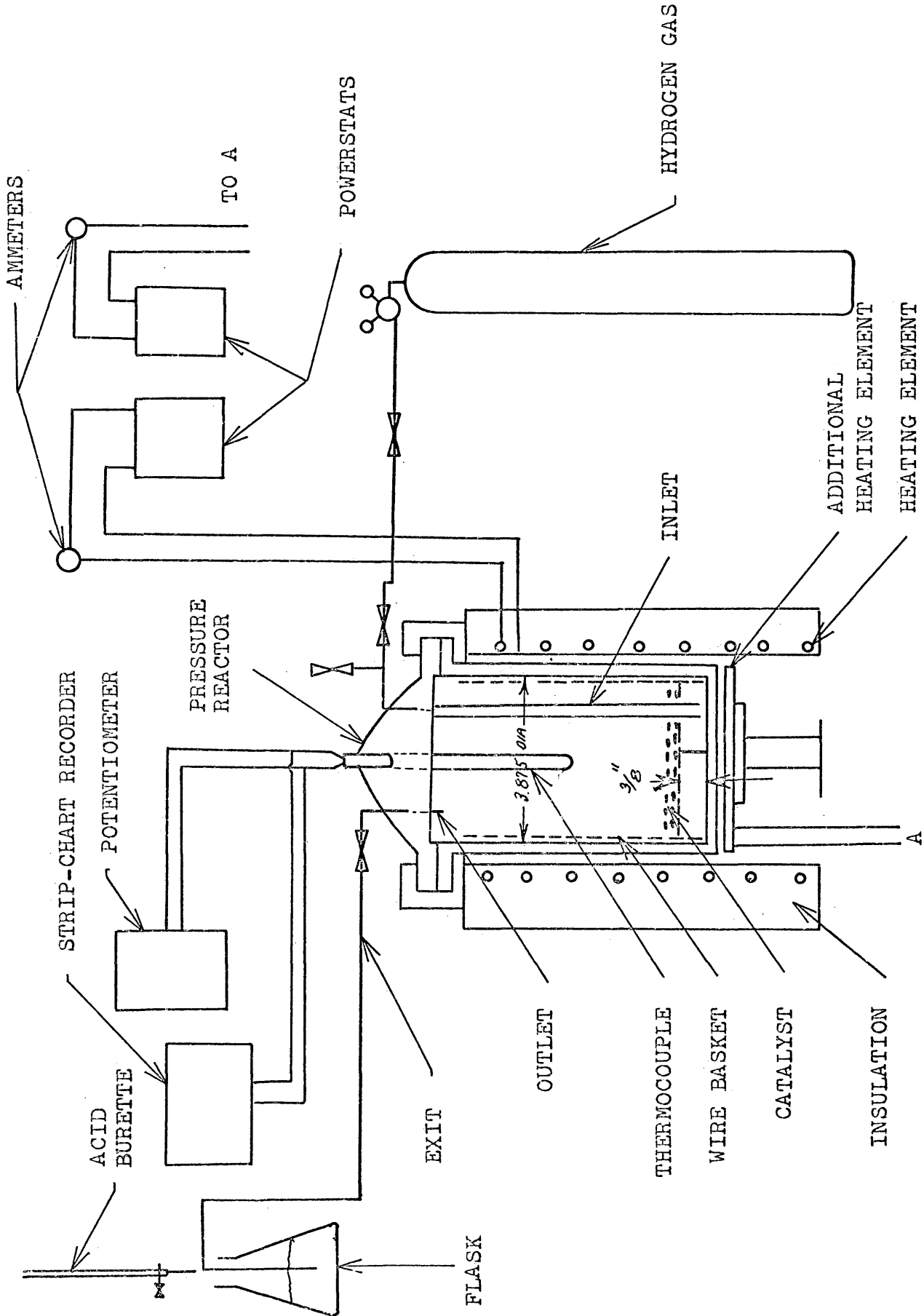


Figure 1: Experimental Apparatus

in the head of the bomb was replaced by a 0.187-in.-o.d ground-ed chromel-alumel thermocouple which could be adjusted to any depth in the bomb. The temperature was monitored on a strip-chart recorder for any irregularities during a run. The measuring thermocouple had an error of $\pm 4^{\circ}\text{F}$.

The volume of the bomb was 1000 ml, and all parts were constructed of 316 stainless steel. A Bourdon gauge, graduated in 20 psi increments with a range from 0 to 2000 psig, was used to measure the operating pressure. The gauge could be read ± 5 psig. The catalyst was placed in a 304 stainless steel 1/16 in. mesh wire basket and was elevated 3/8 in. (0.945 cm) from the bottom of the bomb. The reactant had a depth of 0.33 cm when 25.0 ml of 2,6-lutidine was placed in the pressure vessel.

The oil-pumped hydrogen gas was supplied from a standard cylinder through the inlet gas valve, and gases at the completion of the run were passed through a 250-ml flask containing an acidic solution.

EXPERIMENTAL DESIGN

In order to determine the kinetics of a process, it is necessary to determine the concentration of some reacting species as a function of time, whether in a flow system at steady state or in a batch reactor. Usually, reaction rates are measured under conditions of constant temperature, preferably at two or more temperatures. The rate of a chemical reaction may be followed in many different ways. Samples may be removed from the reaction vessel at intervals, chilled rapidly or quenched chemically, and analyzed.

A batch reactor was used that was operated at various temperatures, pressures, and reaction times. In a batch reactor, the reaction rates were followed by determining the decrease or increase of some reacting specie over some time interval, preferably at isothermal conditions. In most cases, the reaction rate constant is considered independent of the specie concentration, but is influenced by all other variables which influence the rate of reaction. The temperature and pressure of the system which effects the equilibrium can influence the reaction rate constant. When a reaction is a composite of several chemical processes, more than one reaction rate constant may be required to describe the rate, and often, when it is not possible to deter-

mine the individual ones, a pseudo reaction rate constant is determined.

Arrhenius noted that the reaction rate constants followed the relation

$$\frac{\partial (\ln k)}{\partial T} = \frac{E}{RT^2} \quad (\text{Eq. 1}),$$

and can be integrated to the following when the activation energy, E , is assumed constant over the temperature range;

$$k = k_0 e^{-E/RT}. \quad (\text{Eq. 2})$$

Once the rate constants at various temperatures have been determined, the activation energy of the system can be determined from the following equation:

$$\ln (k/k_0) = -E/RT \quad (\text{Eq. 3})$$

The pressure of the system was varied to determine whether there was an effect on the reaction rate constant.

Since the range of hydrocracking is 400 to 800°F and 400 to 1000 psia, the experimental work was designed within this range but not exceeding the limits of the equipment, 750°F and 1000 psig. If the pressure exceeded 800 psig at a temperature of 750°F, the teflon seal was unsatisfactory, and leaks developed.

A 3³ factor experiment was designed initially. This included three different temperatures, pressures, and reaction times throughout the range of temperature and pressures men-

tioned above. Figure 2 shows the graphical representation of the experimental design. Additional points were taken at 700°F - 400 psig and 700°F - 350 psig to substantiate results.

If experiments are repeated several times under the same conditions, the individual observations exhibit an intrinsic variability that cannot be eliminated. This variability is usually called experimental error. In order to determine the variability of the experimentation, two sets of conditions, 600°F - 600 psig - 4 hr and 750°F - 600 psig - 4 hr, were randomly chosen. Four and three replicate runs, respectively, were made. A comparison of the results were made for each of these sets.

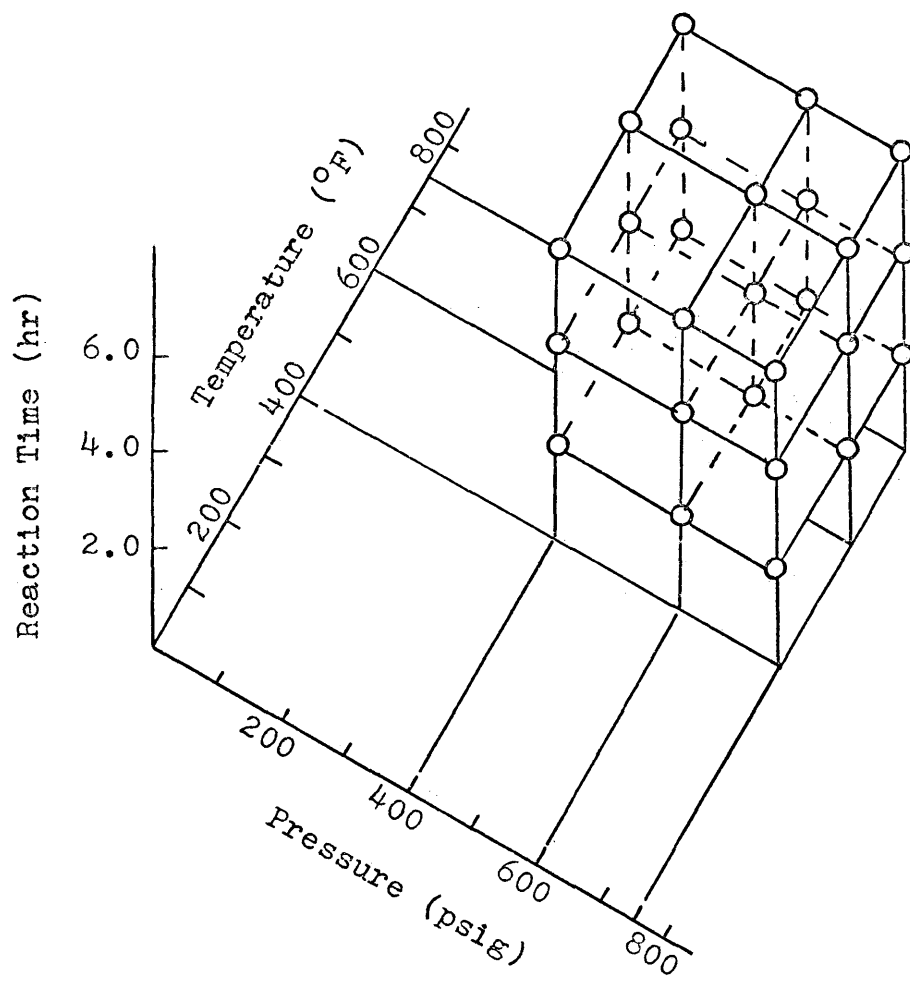


Figure 2: Experimental Design

EXPERIMENTAL PROCEDURE

The experimental procedure can be divided into three areas: preparation of the reactor, actual experimental run, and shutdown of the reactor.

Preparation of the Reactor

Initially, the bomb and catalyst basket were cleaned with acetone and thoroughly dried to insure that no residue was left from previous runs. In each run, 25.0 ml (0.213 gm-moles) of the liquid reactant, 2,6-lutidine, was measured and placed in the reactor. The liquid occupied a depth of 0.33 cm in the reactor. The 2,6-lutidine was of a practical grade with a boiling range of 142 to 144°C. Next, the wire basket containing the catalyst was placed in the reactor.

The catalyst was obtained from the Harshaw Chemical Company, and it was listed as Nickel Tungsten Catalyst Ni-4309 E 1/8". This catalyst contains 10.9-percent W and 5.6-percent Ni. The catalyst was particularly suitable for hydrocracking and denitrogenation; and it was an extruded, porous, cylindrical pellet. Additional specifications and information on surface area, cumulative pore volume, and average bulk density are presented in Appendix I. The catalyst

was never used for more than 18 hours of operation. The ratio of moles of reactant to grams of catalyst was 0.00825 gm-mole/gm catalyst. Only 25.0 grams of catalyst was used for each run.

After the introduction of the catalyst basket, the head of the bomb was tightened down. The hydrogen gas line was connected and the system purged at room temperature for 2 to 3 minutes by passing the gas through the system. The outlet valve was then closed. The pressure in the reaction vessel was allowed to increase until the pressure at room temperature corresponded to the pressure desired at the operating conditions. The room-temperature pressure was calculated through the gas law and compressibility factors. It was also noted whether the vessel was leaking by observing if the pressure dropped.

Actual Experimental Run

During the experimental run, the temperature, pressure, and reaction time were recorded every 20 minutes. The strip-chart recorder was used to measure the initial temperature response. Both Powerstats were operated at maximum voltage at start-up and until the run conditions were attained. The Powerstats were then adjusted to produce the required temperature. In all cases the pressure reactor reached the operating temperature in 15 to 25 minutes, 15 minutes for 400°F and 25 minutes for 750°F. Because of this lag in reaching the operating temperature, the two-hour runs were increased

by 20 minutes. No corrections were made for the four- and six-hour runs.

Shutdown of the Reactor

At the end of a run, the hydrogen gas line was disconnected, and the pressure reactor was placed on a conducting surface with cool air blowing on it. After the bomb reached approximately 350°F, ice was used to reduce the temperature to room conditions. This process took no more than 15 minutes at the highest operating temperature.

Once the pressure reactor cooled to room temperature, the pressure was released, and gases were passed through an acidic solution of sulfuric acid of known concentration. Phenolphthalein was used as the indicator. The amount of acid required to neutralize the basic gases was recorded as the amount of basic gas, which was assumed to be ammonia gas and other basic gaseous amines. The head of the reactor was removed, and the product was placed in screw-cap glass bottles until analyzed.

SAMPLE ANALYSIS

Once the sample was removed from the pressure reactor, it was stored in glass bottles and subsequently analyzed for products. Two techniques of analysis were initially visualized, infrared spectroscopy and gas chromatography. When the first proved to be unsuccessful because of the complex number of compounds formed, the second method was used.

The gas chromatograph used was a Hewlett-Packard Model 5705B. The instrument has a flame detector; thus the sample was burned to carbon dioxide, and the weight percent of each compound could be determined directly by measuring the area under the curve. The instrument has a reproducibility of approximately 5-percent. Appendix II shows the operating conditions of the instrument. The instrument was temperature programmed. The column, a 10-percent UCC, W98-80-100 (gum silicone oil), was six feet long.

The first analysis of samples indicated a large number of compounds, which included all types of hydrocarbons, basic amines, and 2,6-lutidine. It was then concluded that analysis must be made according to groups, which included C₃, C₄, C₅, C₆, C₇, C₈, 2,6-lutidine, and basic material.

Basic material and olefins were identified by reacting

with a dilute sulfuric acid solution. Washing the samples three times with a 10-wt. percent of sulfuric acid, then washing with distilled water, removed the basic material and olefins. A 5-wt. percent of sulfuric acid was used to identify the bases because this concentration will not react with olefins. Basic material was removed, and there was a decrease in the peaks relative to the material that was not affected by the washing. It was concluded this basic material was amines. The 2,6-lutidine was also removed because this is a basic compound. This conclusion is based on the fact that only 2,6-lutidine and hydrogen gas were initially present in the reacting vessel. The 10-percent solution of sulfuric acid reacts with olefins; this reaction was noticed in the analysis of the washed samples. The C₃, C₄, and some C₅'s showed a decrease in peak intensity relative to other peaks. These were not distinguished and classified as olefins, but hydrocarbons.

Amounts of pure known compounds were added to the samples, and an increase in peak intensity identified the unknown peaks. This procedure identified the groups of compounds. The following compounds were used in the identification: pentene-2, n-pentane, n-hexane, heptane-2, n-heptane, cyclohexane, cyclohexene, n-octane, and 2,6-lutidine. These compounds indicate where the forementioned groups will exit in the column. Appendix III presents the residence times of these compounds.

RESULTS

The experimental results can be divided into the five following areas: analysis of the system, conversion of 2,6-lutidine to products, determination of the pseudo order, determination of the activation energy, and the experimental error analysis.

Analysis of the System

The reacting system can be considered under two possible regimes: (A) The reactant is a liquid at the operating temperature and pressure with the gaseous phase at the saturated vapor pressure of the liquid. This gas phase is in contact with the catalyst bed. (B) The reactant is a gaseous vapor contacting the surface of the catalyst. Because of these two possibilities the reaction can be controlled by mass transport from the liquid to the catalyst surface. Mass transfer from the liquid to the catalyst surface assumes that the reactant reacts immediately at the surface of the catalyst. This is characterized by (A). This is diffusion controlling outside the porous catalyst.

Because of the porous nature of the catalyst, there can be controlling diffusion within the pellet. Diffusion within the pellet could apply in either case (A) or (B). There

also could be a combination of both of these if the resistances to mass transfer within the catalyst and from the liquid to the pellet are of the same magnitude and are controlling. Transfer from the liquid to the catalyst deals with ordinary diffusion, and the transfer within the catalyst is characterized by diffusion, but the effectiveness factor is a measure of its magnitude or importance.

In order to determine the phase of the reactant in the reaction vessel, a phase diagram of the pure compound was prepared. The calculations are shown in Appendix V, and Figure 3 shows the results. As can be seen from Figure 3, some runs were made both in the liquid and vapor regions. Appendix IV gives the vapor pressure at various temperatures. The data were taken from Timmermans (12) and extrapolated to higher temperatures.

Since liquid and vapor were present, mass transport from the liquid to the catalyst surface, assuming instantaneous reaction at the catalyst's surface was 0.544 gm-moles/hr at 600°F-400 psig and 0.0831 gm-moles/hr at 400°F-600 psig for the two extremes in the liquid region (see Appendix VI for calculations). At the lower rate, 0.1662 gm-moles would be reacted in 2 hours. Experimental results indicate only 0.0106 gm-moles have reacted. This fact indicates that mass transport to the pellet is not controlling.

The transfer within the catalyst has to be considered to determine whether the actual activation or an apparent

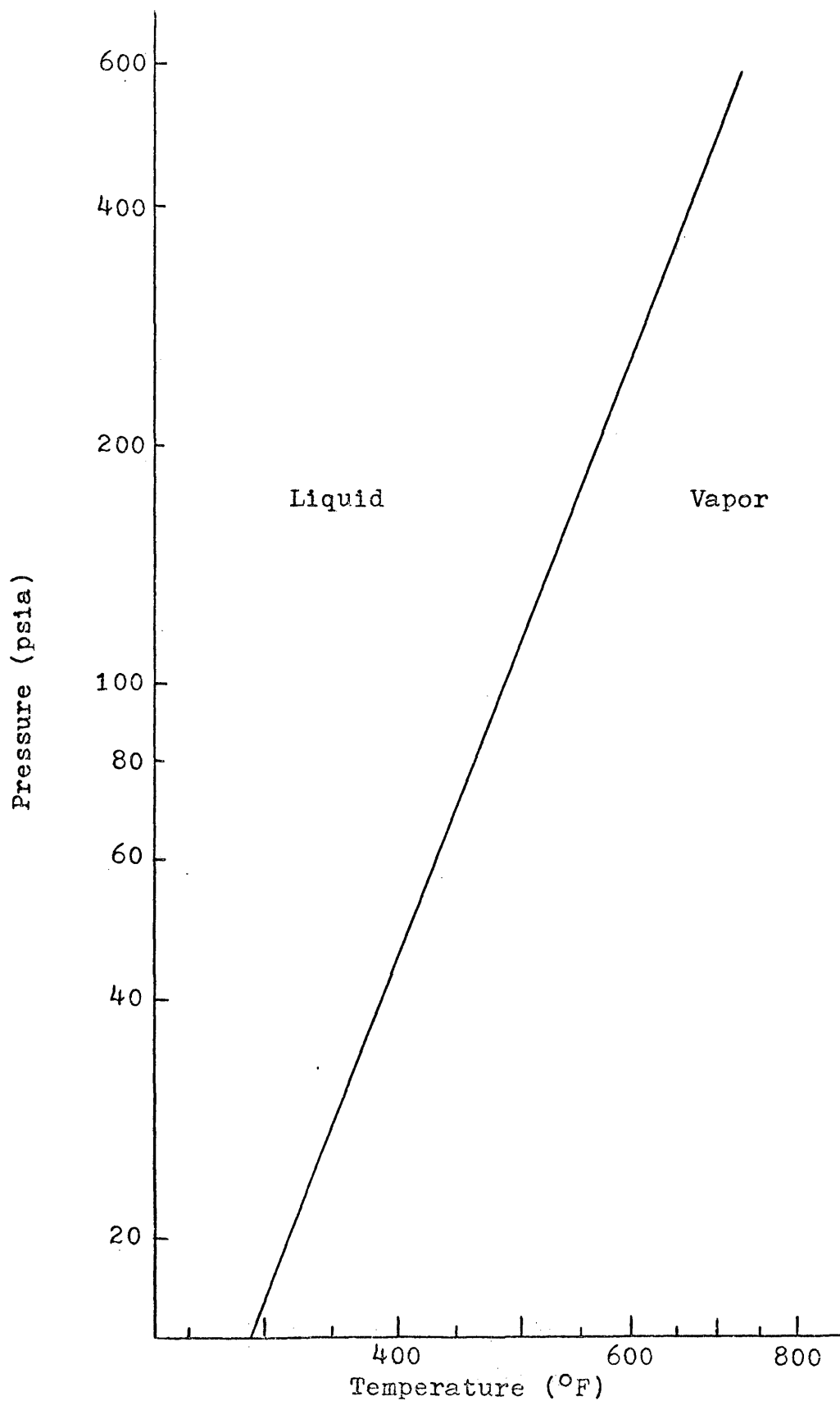


Figure 3: Phase Diagram for 2,6-lutidine

activation energy is determined. The effectiveness factor, η , for the system was determined to be approximately 1.0 (see Appendix VI for calculations). According to the criteria presented in Satterfield and Sherwood (13), $\eta e^{s\beta/(p+1)} < 1.0$. This calculation shows that the reaction was not diffusion controlled within the catalyst and that the activation energy was the actual energy determined by experimental results.

Conversion of 2,6-lutidine to Products

Figures 4 through 6 show the formation of total hydrocarbons from liquid reactant (2,6-lutidine) versus reaction time for the various temperatures and pressures as parameters. Appendix VII shows all the raw data from the runs and weight percent in the analysis of the various groups. These results indicate an increase of total hydrocarbons as the temperature and pressure were increased. Results at 600°F-400 psig and 400°F-400 psig do not support this conclusion but are erroneous because of the experimental error, since a small amount of hydrocarbons were formed and since a great amount of variance was associated with the small weight percent. At 750°F, for pressures above 600 psig and reaction time above 4 hours, over 70-wt. percent total hydrocarbons were formed.

Determination of the Pseudo Order

The order of the reaction of 2,6-lutidine can be determined by plotting the concentration as a function of reaction time by means of the two following equations:

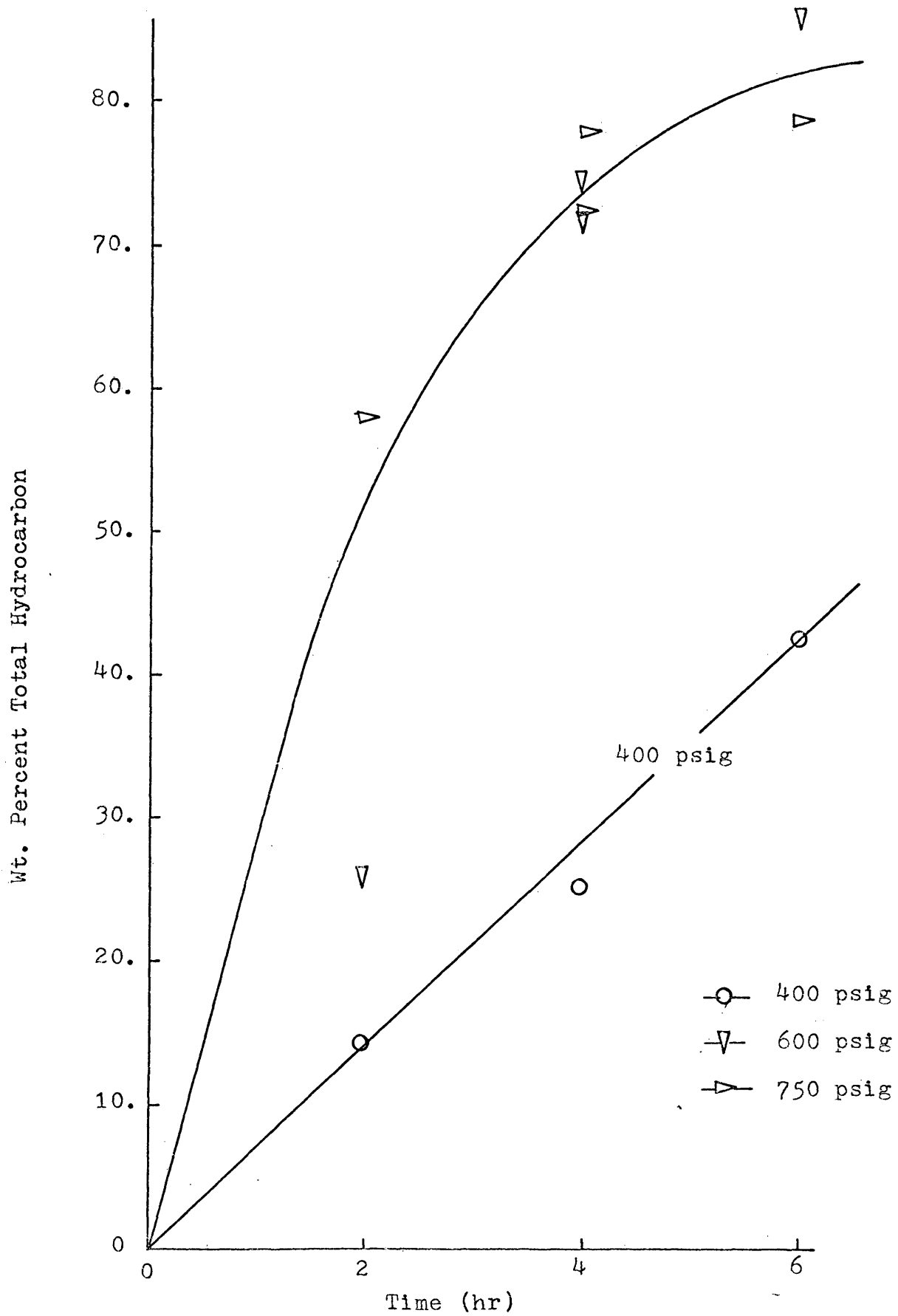


Figure 4: Total Hydrocarbon Wt. Percent at 750°F

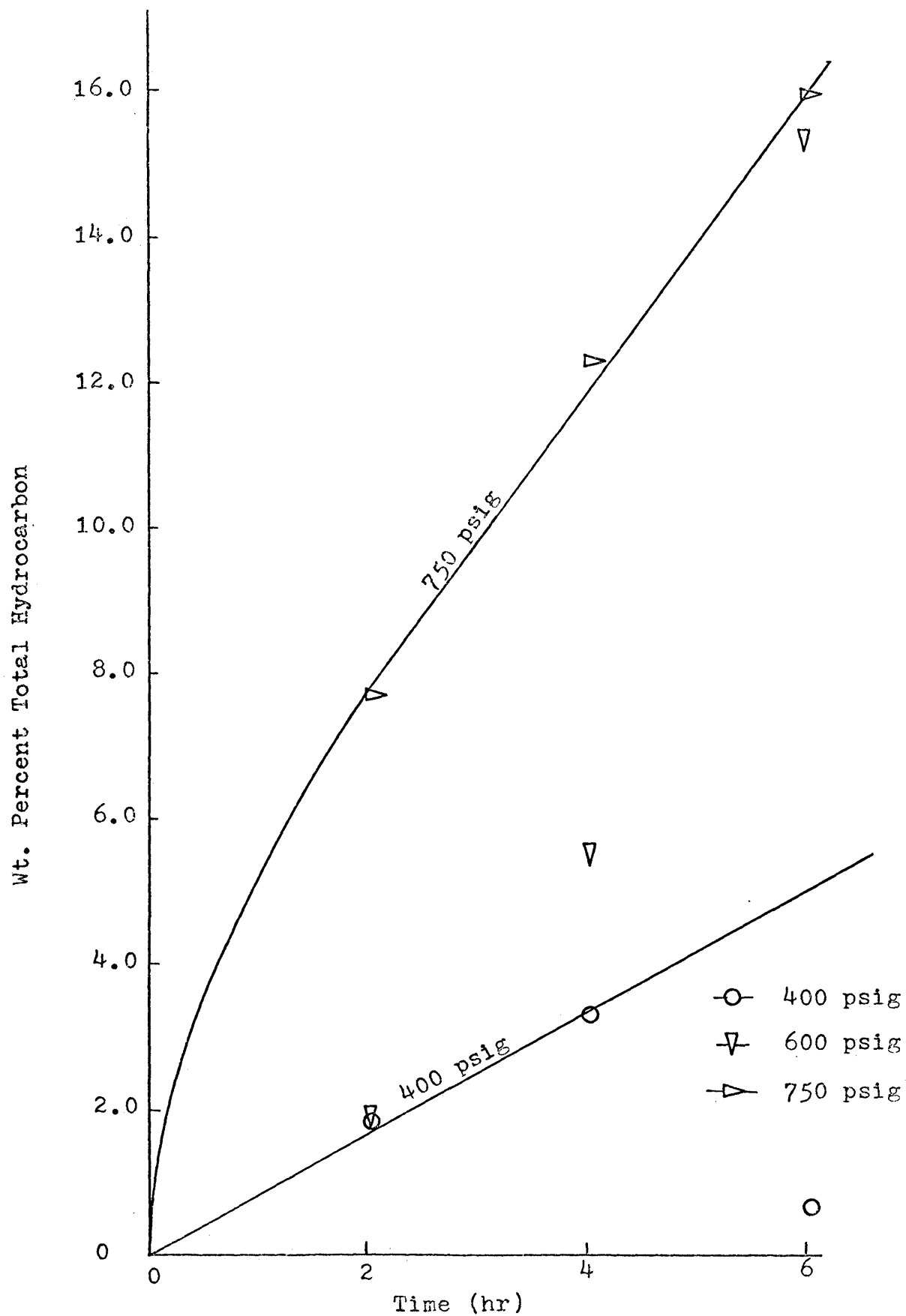


Figure 5: Total Hydrocarbon Wt. Percent at 600°F

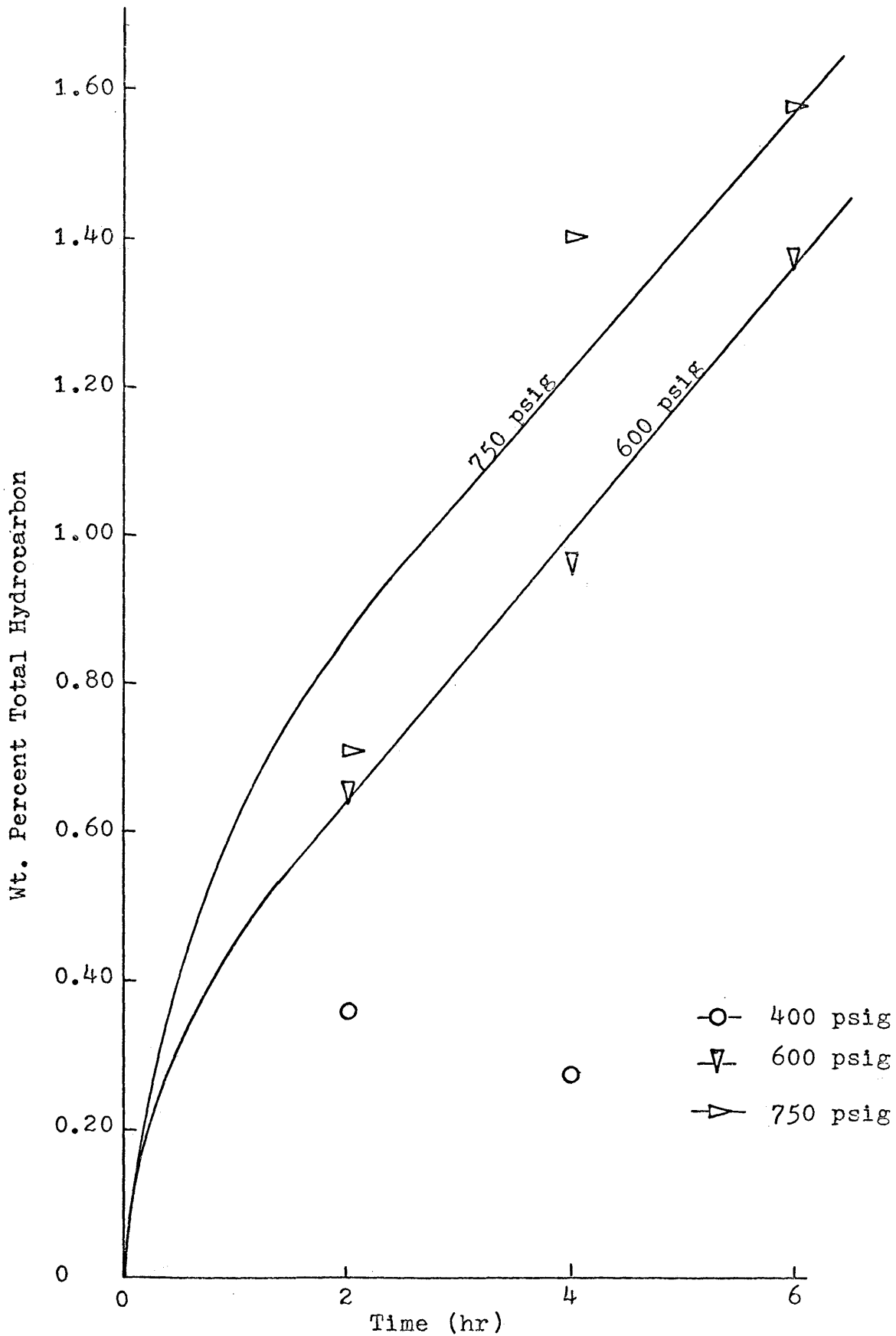


Figure 6: Total Hydrocarbon Wt. Percent at 400°F

$$(1/C_t)^{n-1} - (1/C_o)^{n-1} = k(n-1)t, \quad n \neq 1,$$

$$- \ln (C_t/C_o) = kt, \quad n = 1,$$

where n is the order of the reaction. The experimental data best fit the first-order equation,

$$- \ln (C_t/C_o) = kt.$$

Figures 7 through 17 show the results. As mentioned in the experimental design section, the reaction rate constant, k , is a function of temperature if the Arrhenius dependency holds. Table I shows the reaction rate constants that were calculated from the slope of the line. The reaction rate constant was determined by a least-squares fit of a linear equation where a constraint was placed on the equation. The constraint was at the reaction time equals zero, $\ln (C_t/C_o)$ equals zero. Appendix VIII shows how the concentration of 2,6-lutidine was determined. The reaction rate constant increases as the temperature increases; there was also an increase in k when the pressure was increased, but one could not distinguish whether it was an experimental error or an actual phenomena of the system. When the pressure was changed, the concentrations of the components changed, but this change should not affect the rate constant, since it is usually only a function of temperature.

Determination of the Activation Energy

The reaction was determined not to be diffusion control-

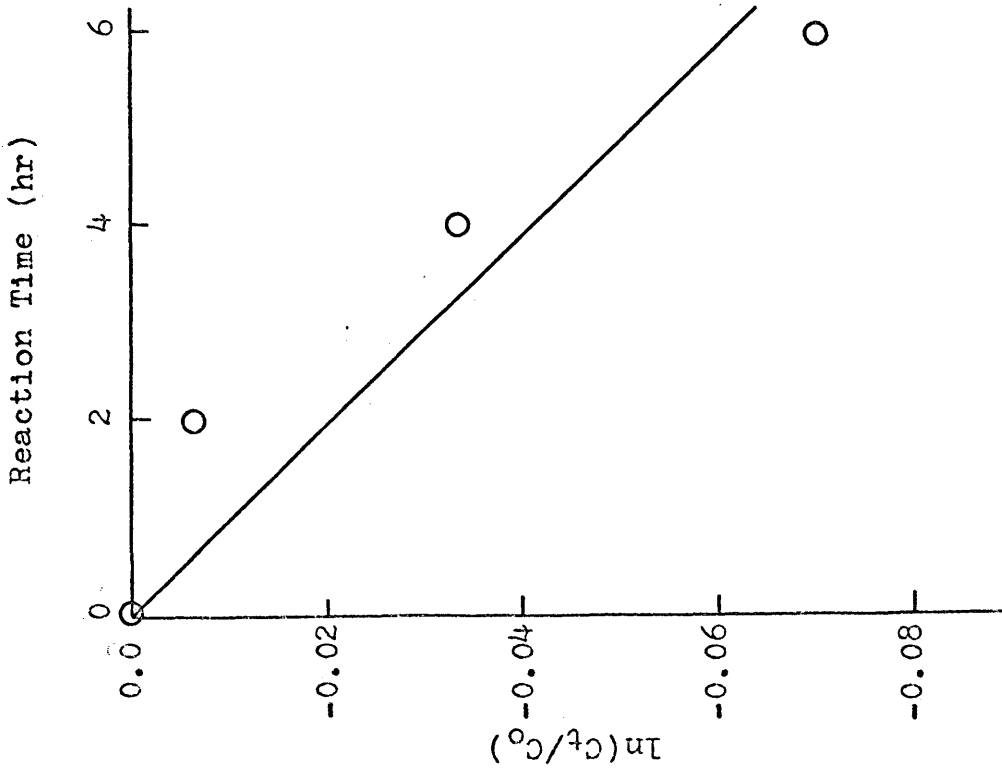


Figure 7: Concentration Data at
400°F-400 psig
2,6-Lutidine

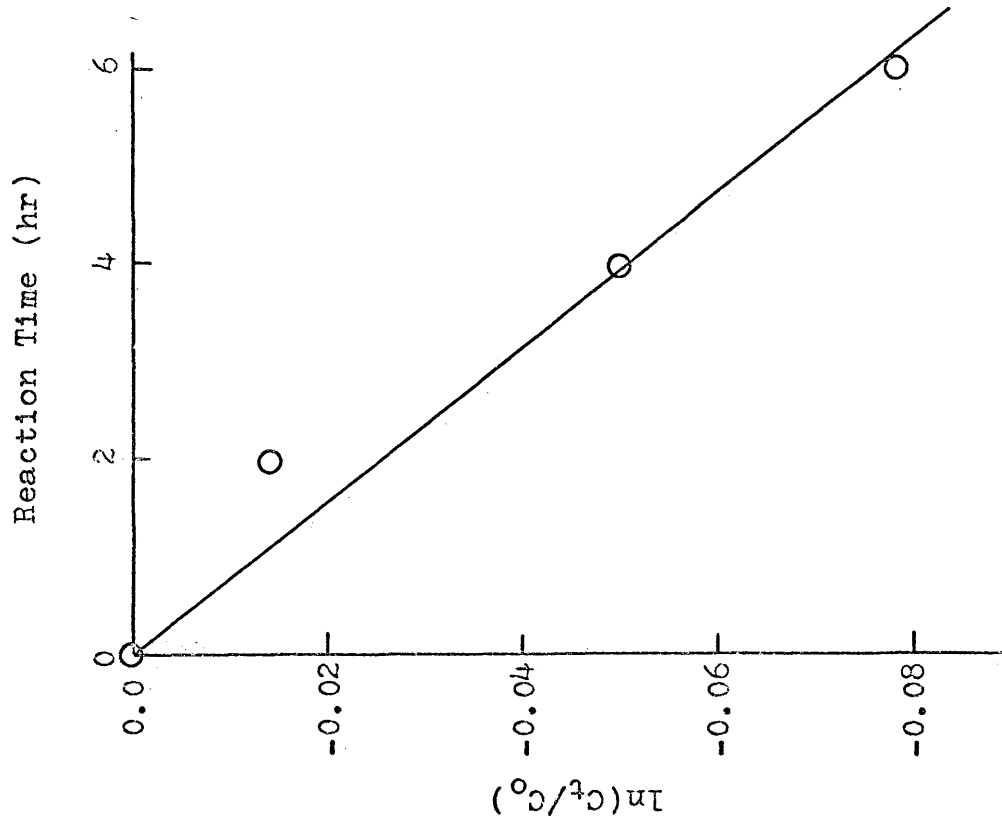


Figure 8: Concentration Data at
400°F-600 psig
2,6-Lutidine

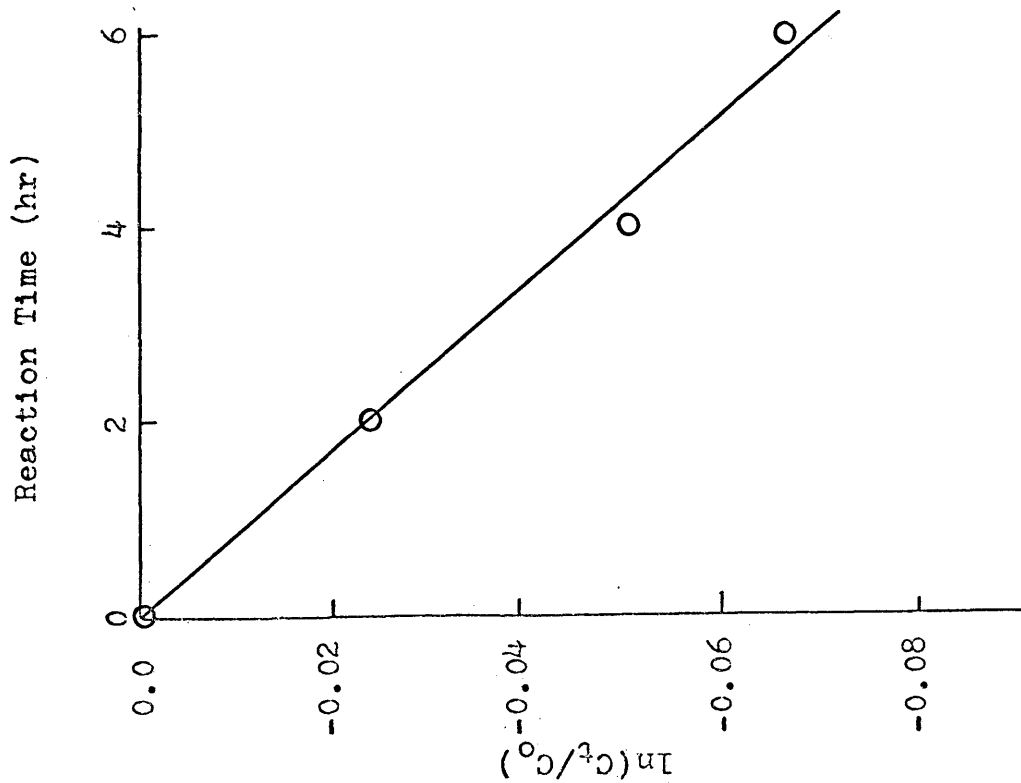


Figure 9: Concentration Data at
400°F-750 psig
2,6-Lutidine

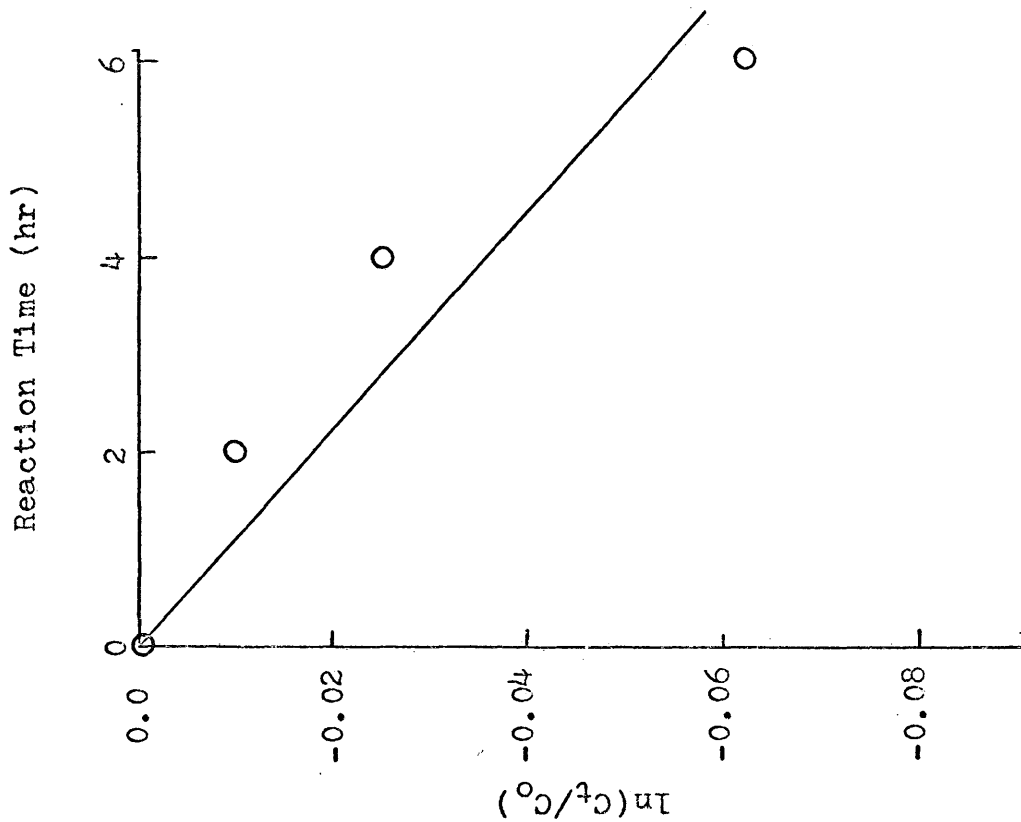


Figure 10: Concentration Data at
600°F-400 psig
2,6-Lutidine

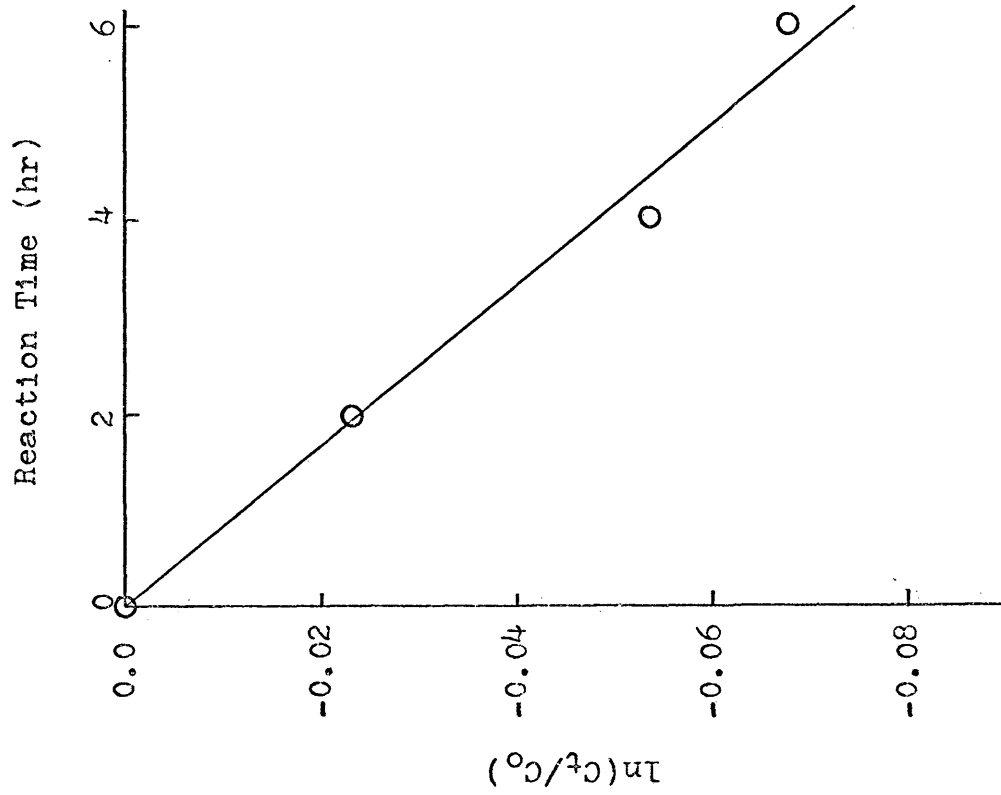


Figure 12: Concentration Data at
600°F-750 psig
2,6-Lutidine

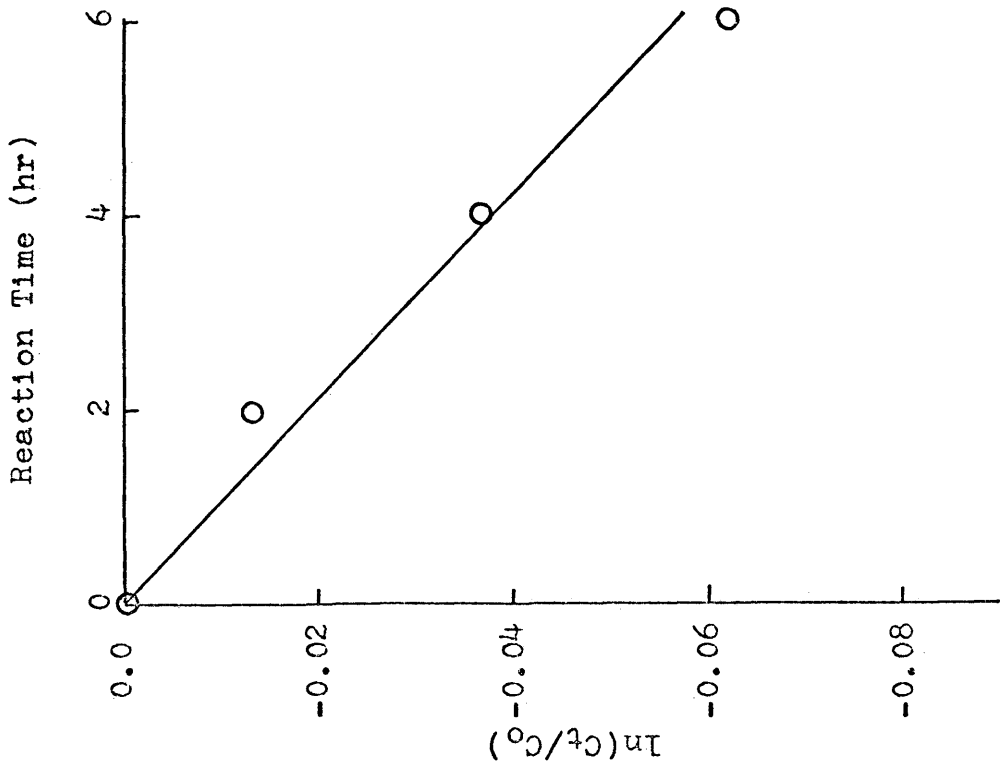


Figure 11: Concentration Data at
600°F-600 psig
2,6-Lutidine

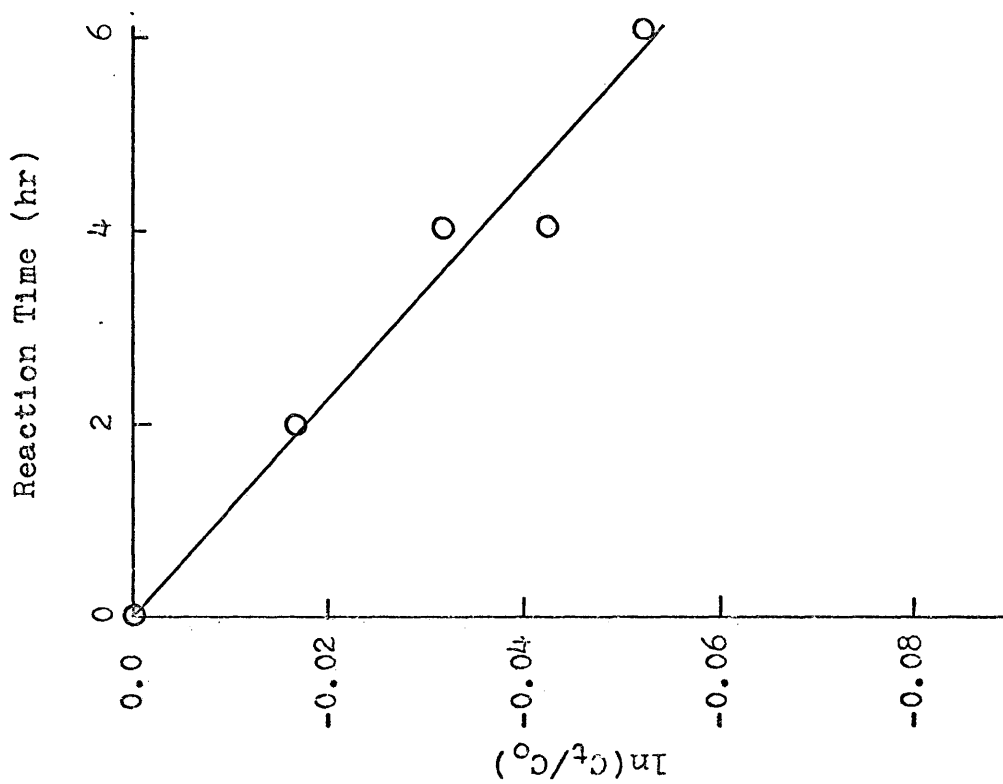


Figure 14: Concentration Data at
750°F-600 psig
2,6-Lutidine

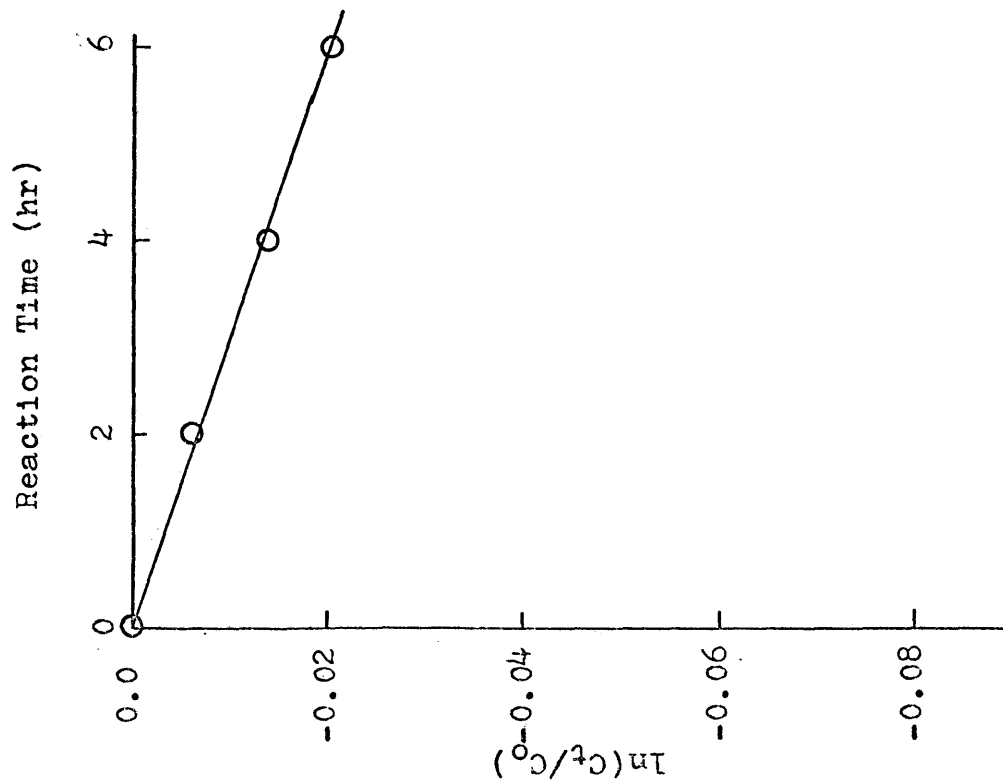


Figure 13: Concentration Data at
750°F-400 psig
2,6-Lutidine

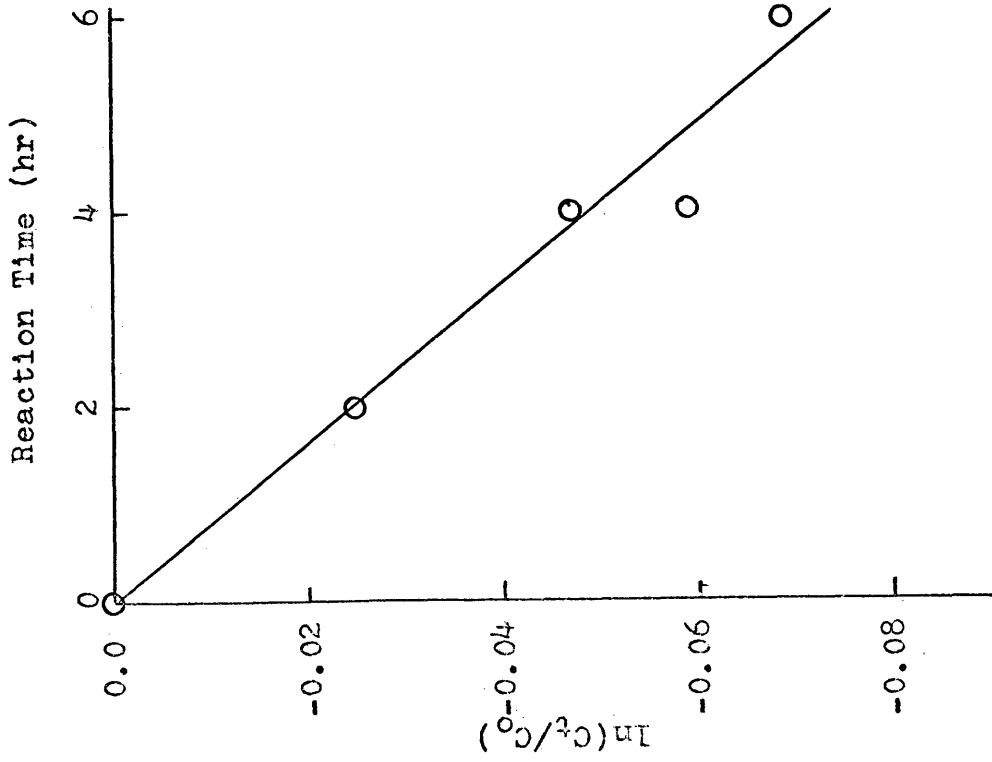


Figure 15: Concentration Data at 750°F-750 psig 2,6-Lutidine

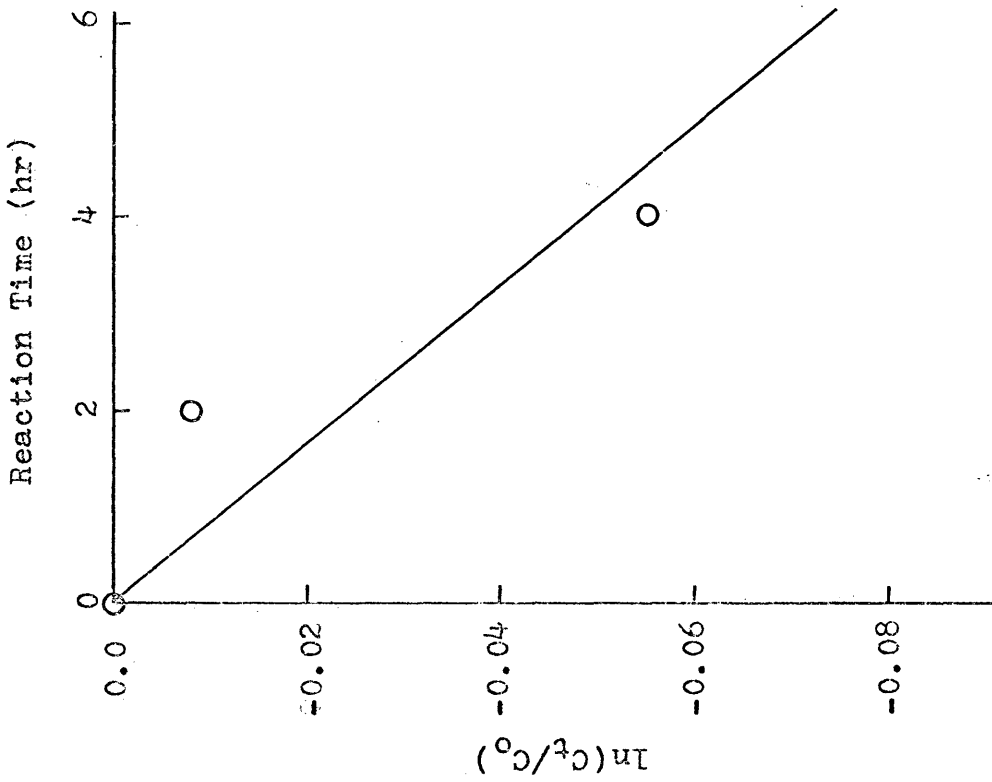


Figure 16: Concentration Data at 700°F-400 psig 2,6-Lutidine

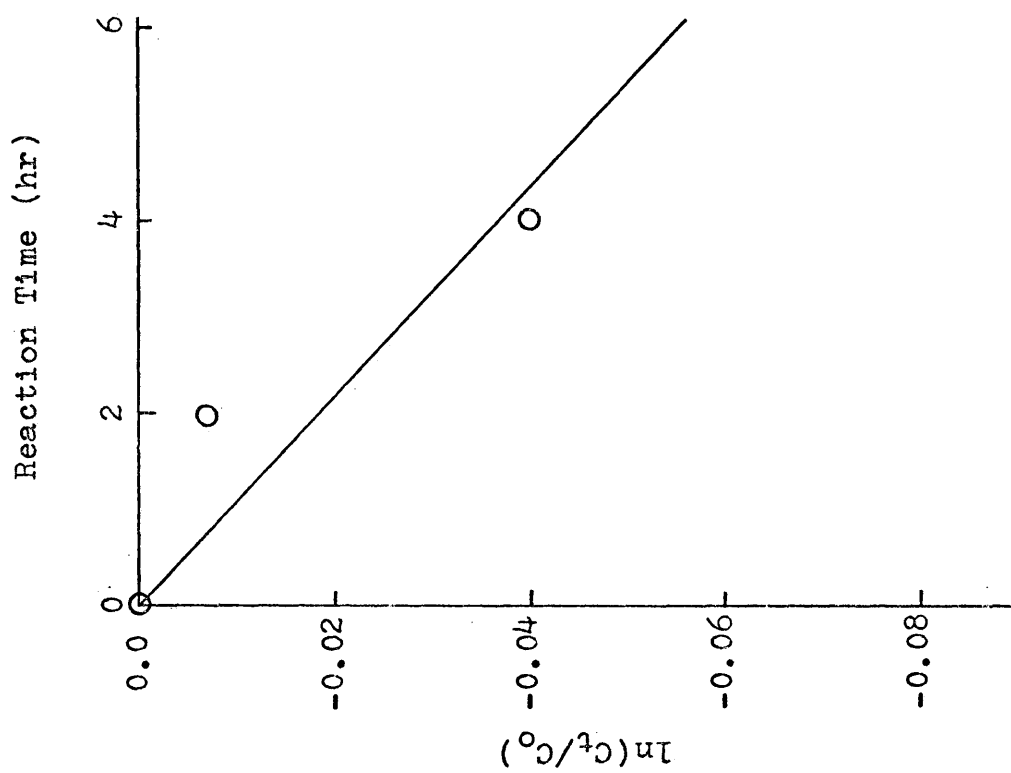


Figure 17: Concentration Data at
700°F-350 psig
2,6-Lutidine

TABLE IExperimental Reaction Rate Constants (hr^{-1})

<u>Temperature ($^{\circ}\text{F}$)</u>	<u>Pressure (psig)</u>			
	350	400	600	750
400	---	0.0102	0.0128	0.0116
600	---	0.0363	0.0377	0.0482
700	0.0924	0.119	---	---
750	---	0.170	0.448	0.611

led either in the liquid or gaseous phase, or in the porous catalyst; therefore the apparent activation energy was the actual activation energy. Figure 18 shows the rate constant as a function of temperature with pressure as a parameter. Also included on the figure is the plot of the data by a least-squares fit when the parameter, pressure, was neglected. The run at 700°F-350 psig was not used in these calculations but is shown on the figure. Table II shows the pre-exponential of the rate constant, k_0 , and the activation energies that were calculated by a least-squares fit from the data.

Analysis of Experimental Error

The errors in this presentation can be divided into two groups: the inherent variability of the experimental results (experimental error) and the error introduced because of the polynomial fitting of data.

In order to determine the inherent variability, four replicate runs were made at 600°F-600 psig - 4 hr, and three replicate runs were made at 750°F-600 psig - 4 hr. Results of these are shown in Appendix IX. Many models could be applied to this situation, and all could possibly describe some aspect of the problem in the analysis of variance. Since the raw data were converted to weight percent of the constituents in the sample, the intrinsic variability was based on the weight-percent conversion of the 2,6-lutidine and the weight percent of the formation of products. The simplest model to describe the complex situation was described by the following

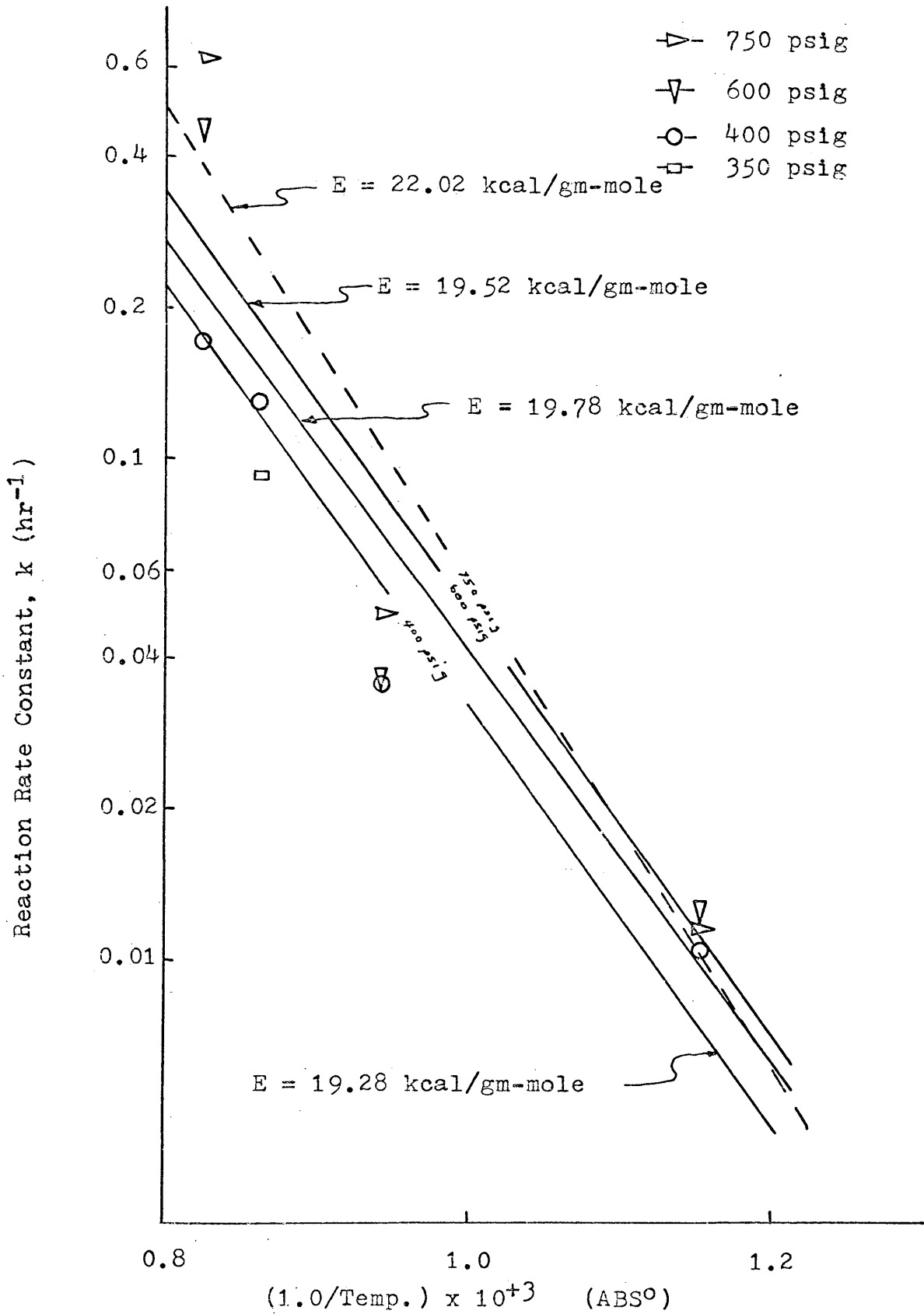


Figure 18: Reaction Rate Constant as a Function of Temperature

TABLE II

Activation Energies and Pre-exponentials

<u>Pressure</u> <u>(psig)</u>	<u>k_o</u> <u>(hr⁻¹)</u>	<u>Activation Energy</u> <u>(kcal/gm-mole)</u>
750	6.59 x 10 ¹⁸	22.02
600	4.25 x 10 ¹⁵	19.52
400	2.51 x 10 ¹⁴	19.28
overall	3.35 x 10 ¹⁴	18.78

equation:

$$W = \sum_1^n C_k \bar{Y}_k, \quad \bar{Y}_k = \frac{\sum Y_{ki}}{n}$$

where W is the "total worth"; Y_{ki} is a random variable, the weight percent of 2,6-lutidine, or the weight percent of one of the groups, $C_3, C_4, C_5, C_6, C_7, C_8$, or bases; and C_k is a weighting function, a constant that could be considered the profit per weight percent. This was assumed to be a unit profit (\$1 per wt. percent) and varied to determine the effect of C_k for each group since no economic data were available to determine the importance of each group.

From this model, a mean expected profit could be calculated along with the expected range of this profit that could be expressed by the variability. This expected range is solely determined from the random errors due to the variability of the experimentation. The random variable, Y_{ki} , should not be considered independent since the amount of products formed depends on the amount of 2,6-lutidine reacted. The variance of the model was determined from the following equations:

$$\sigma_w^2 = \text{var } w = \sum C_k^2 \sigma_k^2 + 2 \sum_{k \neq k'} C_k C_{k'} E[(Y_{ki} - \bar{Y}_k)(Y_{k'i} - \bar{Y}_{k'})]$$

$$\sigma_w^2 = \text{var } w = \sum C_k^2 \sigma_k^2 + 2 \sum_{k \neq k'} C_k C_{k'} \rho_{kk'} \sigma_k \sigma_{k'}$$

where σ_k^2 is the variance of the random variable, Y_{ki} , and the term, $\sum \sum C_k C_{k'} \rho_{kk'} \sigma_k \sigma_{k'}$ is the covariance term caused by the interaction of the random variables. The value of the covariance term can be determined from the following expression:

$$r'_{kk'} = \rho_{kk'} \sigma_k \sigma_{k'} = n \sum Y_{ki} Y_{k'i} - (\sum Y_{ki})(\sum Y_{k'i})$$

Appendix IX shows the calculation of the variance and covariance terms.

The value of the standard deviation of the "total worth" was \$12.68 and \$8.88, using the weighting functions as a dollar profit per weight percent, respectively, for each set of runs. A confidence limit can be expressed by the following statement: For a total profit from the samples of \$100 per pound of sample or 100-weight percent, the profit or weight percent will vary between \$100 \pm \$12.68 (100-wt. percent \pm 12.68 percent) and \$100 \pm \$8.88 (100-wt. percent \pm 8.88 percent), respectively. This is true 70-percent of the time and is one standard deviation. Included in Appendix IX is a table showing the values of the "total worth" variance at the various profits realized from each component. The equations in Appendix IX are expressed as a function of unit profit.

Table III shows the individual standard deviations and confidence intervals at a 95-percent probability. This is

approximately 1.5 standard deviations for four replicate runs and 2.5 standard deviations for three replicate runs. It should be noted that the confidence intervals neglect the interaction. The individual compounds are not independent, and the expected mean value of one compound effects the expected mean value of another compound. This was the reason why the covariance had to be determined.

Figures 7 through 18 were determined by a least-squares fit of a first-order polynomial. Appendix X presents the data that were used to determine the intercepts and the slopes (rate constants). Figure 19 shows the weight percent products versus hours of catalyst use. Appendix XI presents the data. Figure 19 shows whether the activity of the catalyst has changed. If the activity of the catalyst has not changed, the slope of the lines should be about zero.

For 2,6-lutidine, if the slope is positive, less of the reactant is being converted, a fact indicating that the activity of the catalyst is decreasing gradually. For total hydrocarbons, if the slope is negative, less of the reactant is being converted to hydrocarbons, a fact indicating that the activity of the catalyst is decreasing. Appendix XI shows the data and the results obtained for the slopes, using a first-order polynomial fit.

TABLE III

Standard Deviation of Replicate Runs

Conditions: 750°F-600 psig - 4 hr.

Number of Runs: 3

<u>Compound Groups</u>	<u>Mean (\bar{Y}_k)</u>	<u>Standard Deviation (S)</u>	<u>Confidence Interval 95% Probability</u>
C ₃	0.027	0.0231	+ 0.0578 -
C ₄	0.327	0.162	+ 0.405 -
C ₅	0.133	0.116	+ 0.290 -
C ₆	0.593	0.485	+ 1.21 -
C ₇	73.813	1.705	+ 4.26 -
C ₈	3.873	3.190	+ 7.98 -
2,6-lutidine	12.276	2.205	+ 5.51 -
Bases	8.963	3.72	+ 9.30 -

Conditions: 600°F-600 psig - 4 hr.

Number of Runs: 4

<u>Compound Groups</u>	<u>Mean (\bar{Y}_k)</u>	<u>Standard Deviation (S)</u>	<u>Confidence Interval 95% Probability</u>
C ₇	4.40	1.565	+ 2.35 -
C ₈	0.680	0.149	+ 0.222 -
2,6-lutidine	87.93	2.05	+ 3.08 -
Bases	6.975	0.904	+ 1.35 -

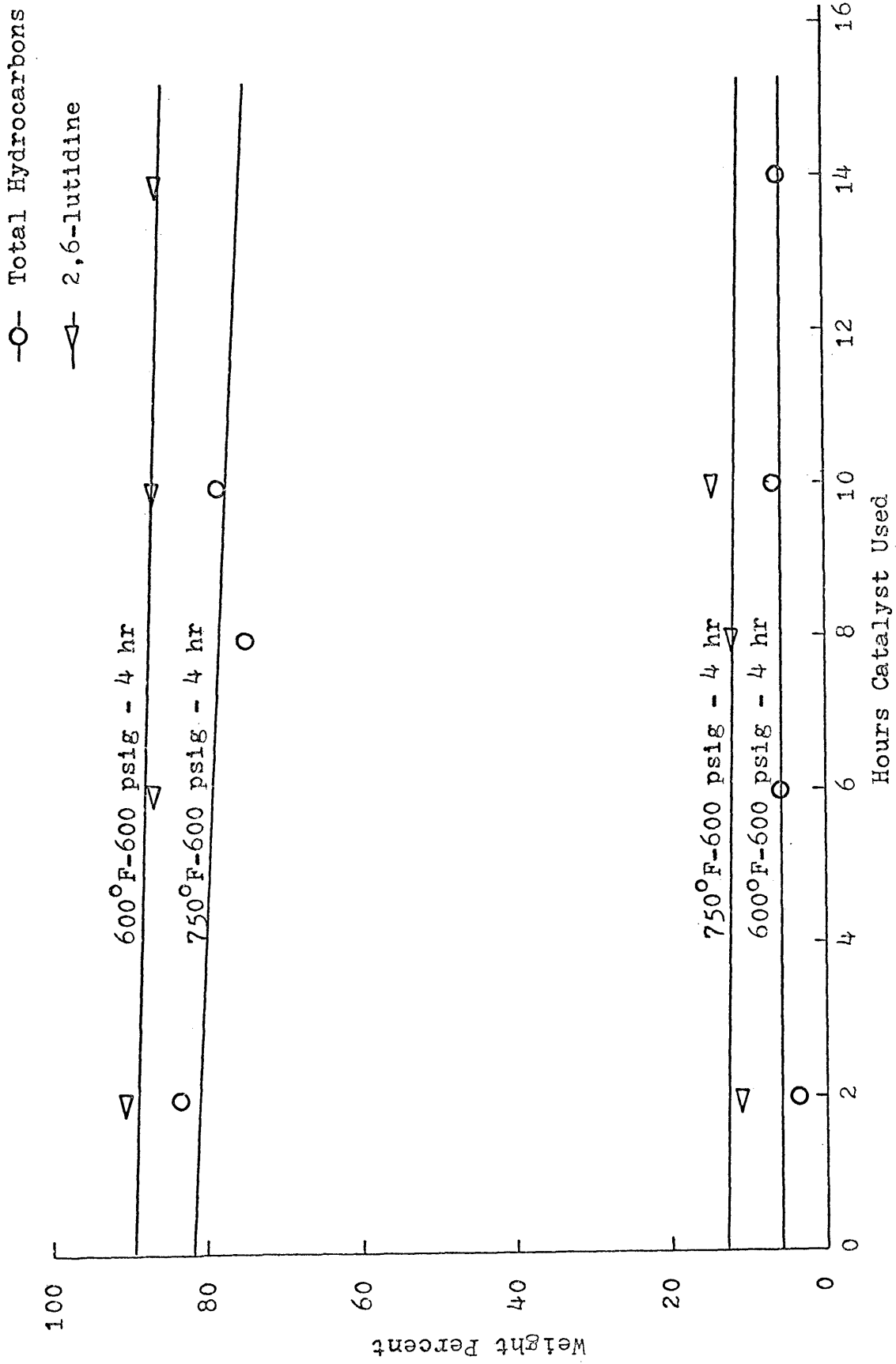


Figure 19: Catalyst Activity

CONCLUSIONS

The hydrocracking of 2,6-lutidine occurred in the range of temperatures and pressures studied. The conversion of 2,6-lutidine to hydrocarbons was over 70-wt. percent at temperatures, pressures, and reaction times above 750°F, 600 psig, and 4 hours. This is illustrated in Figure 4. Many hydrocarbon compounds were formed at these conditions which possibly indicates thermocracking since the reaction of 2,6-lutidine with hydrogen would ideally form n-heptane as the saturated hydrocarbon if hydrocracking occurred. The conditions stated above were suitable for low molecular weight hydrocarbons to be thermally cracked.

The data, concentration of 2,6-lutidine versus reaction time, were plotted; and these data best fit the first-order model,

$$- \ln (C_t/C_o) = kt.$$

The reaction mechanism was a pseudo first-order in 2,6-lutidine. This rate of disappearance of 2,6-lutidine can be expressed by the following:

$$-(dn/dt) = V_R k C_t.$$

The power that the concentration of 2,6-lutidine is raised to is the order of the reaction. This was determined to be one (1.0). The reaction rate constant, k , can be expressed by the following equation:

$$k = k_0 \exp -E/RT, \text{ a function of temperature.}$$

By a least-squares fit, the pre-exponential, k_0 was determined to be $3.35 \times 10^{14} \text{ hr}^{-1}$ for the overall data. Table II shows that the pre-exponential ranged from $2.51 \times 10^{14} \text{ hr}^{-1}$ to $6.59 \times 10^{18} \text{ hr}^{-1}$. This large deviation was caused by the large experimental error.

The reaction mechanism was concluded to be very complex at the higher temperatures, and no attempt was made to determine this mechanism. At the lower temperatures, few compounds were formed; but since hydrocracking is not done at these low temperatures, a complete study was not made.

The system was not diffusion controlled either in the porous catalyst or in the transfer of reactant to the catalyst surface. The apparent or the experimental activation energy is the actual activation energy. For the first-order model, an overall activation energy of 18.78 kcal/gm-mole was calculated. Table II shows that the activation energy varied from 22.02 kcal/gm-mole to 18.78 kcal/gm-mole. The overall activation energy was lower because there were more observations at 400 psig, four rather than three. This extra weighting decreased the slope. Since experimental uncertain-

ty was large, as illustrated by Table III, it could not be determined conclusively whether pressure actually affected the rate constant and thus the activation energy. The rate constant can be expressed by the following equation:

$$k = 3.35 \times 10^{14} \exp -18.78/RT \quad (\text{hr}^{-1}),$$

for the temperature range of 400°F to 750°F.

The Harshaw Nickel Tungsten Catalyst Ni-4309 E 1/8", a porous, extruded, cylindrical pellet, was suitable for hydrocracking 2,6-lutidine, and the catalyst activity showed no decrease in activity when used for at least 18 hours.

Figure 19 and Appendix XI show that, for three cases, runs at 600°F-600 psig - 4 hr, both the 2,6-lutidine and total hydrocarbons had slopes of -0.4278 and + 0.4974, respectively, a result which indicated that the activity was not decreasing. The slopes would be positive for 2,6-lutidine and negative for total hydrocarbons if the activity was decreasing. In the third case at 750°F-600 psig - 4 hr, the slope of the 2,6-lutidine was -0.1145.

The run at 750°F-600 psig - 4 hours for total hydrocarbons had a slope of -0.8397, indicating a decrease in activity, but the data plotted indicated that the point at 2 hours was 83.44-wt. percent. Table III shows that the confidence interval at 95-percent probability was \pm 4.26-percent for the C₇ group with a mean of 73.81-wt. percent. By including the other compounds classified as total hydrocarbons, a guess of

the deviation would be about ± 6.0 -percent. With the overall expected total hydrocarbon mean of 78.766-percent, the 95-percent confidence interval would be 72.766-percent to 84.766-percent. From this interval, 83.44-percent lies within it; and because of the uncertainty in the experimentation, the slope was determined to be negative. From this data the activity of the catalyst showed no decrease.

Using a model called "total worth", for calculating the expected variance in profit if the compounds were sold at the price of \$1 per weight percent of each compound, the range of profit for an expected mean value of profit of \$100 was calculated to be $\pm \$12.68$ and $\pm \$8.88$. This is one standard deviation, and from this the range of profit can be expected to fall in this range 70-percent of the time. By using a 99-percent confidence interval for the standard deviation of \$12.68, the profit would be expected to vary from \$64 to \$136, a variation which indicates that the experimental uncertainty was large.

RECOMMENDATIONS

Additional studies could be made by using various ratios of reactant to catalyst. The catalyst could be changed to other materials used in hydrocracking such as cobalt molybdate. Other nitrogen-containing compounds that are found in abundance in shale oil could be used. Two such compounds are 2,4,6-Trimethylpyridine and 2,4-Dimethylpyridine (14).

Studies could be made at lower temperatures and pressures where thermocracking does not occur to determine the exact mechanism. The conditions would be below 400°F and 400 psig.

The experimental apparatus could be set up as a micro-flow reactor. A small tubular reactor packed with catalyst could be operated so that the products from the exit stream could be directly injected into the analyzing equipment, the chromatograph. This equipment could allow better control and possibly decrease the experimental error.

APPENDIX I

Catalyst Specifications

Harshaw's Nickel Tungsten Catalyst Ni-4309 E 1/8"

W, %	10.9
Ni, %	5.6
Surface Area, m ² /g	150
Cumulative Pore Volume, cc/g	
Up to 120 Å Dia.	.20
Up to 200 Å Dia.	.24
Up to 350 Å Dia.	.27
Up to 700 Å Dia.	.30
Up to 1,000 Å Dia.	.31
Up to 10,000 Å Dia.	.46
Up to 175,000 Å Dia.	.47
ABD, packed, g/cc	.85
Average Crushing Strength, Lbs.	21

APPENDIX IIOperating Conditions of the
Hewlett-Packard Model 5705B
Chromatograph

Column material	10% UCC(gum silicone)
Column length	6 ft.
Injection port temperature	180°C.
Flame detector temperature	300°C.
Post injection interval	5 min.
Upper limit interval	0 min.
Rate temperature increase	20°C./min.
Lower temperature limit	20°C.
Upper temperature limit	275°C.
Carrier flow rate	20 ml./min.
Carrier gas	Helium
Attenuation (initial)	16
Range (initial)	10 ³

APPENDIX IIIResidence Times of Hydrocarbons
in the Chromatograph

<u>Compound</u>	<u>Time (min)</u>
pentene-2	2.5
n-pentane	4.0
n-hexane	4.35
heptane-2	6.3
n-heptane	8.0
cyclohexane	8.9
cyclohexene	11.4
n-octane	14.2
2,6-lutidine	16.8

APPENDIX IV

Saturated Vapor Pressure

2,6-Lutidine (15)

<u>T°C</u>	<u>P mm Hg</u>	<u>T°C</u>	<u>P mm Hg</u>
144.300	765.22	125.637	447.22
143.917	757.30	122.877	410.92
142.917	735.65	120.305	379.30
141.850	709.02	116.979	341.36
139.909	678.16	113.949	309.25
138.750	656.24	112.351	293.55
136.638	618.10	108.211	255.69
135.162	592.55	105.723	234.75
133.486	564.22	100.326	194.32
131.655	535.01	95.180	161.30
129.190	497.55	83.938	105.01
127.495	473.01	79.290	87.06

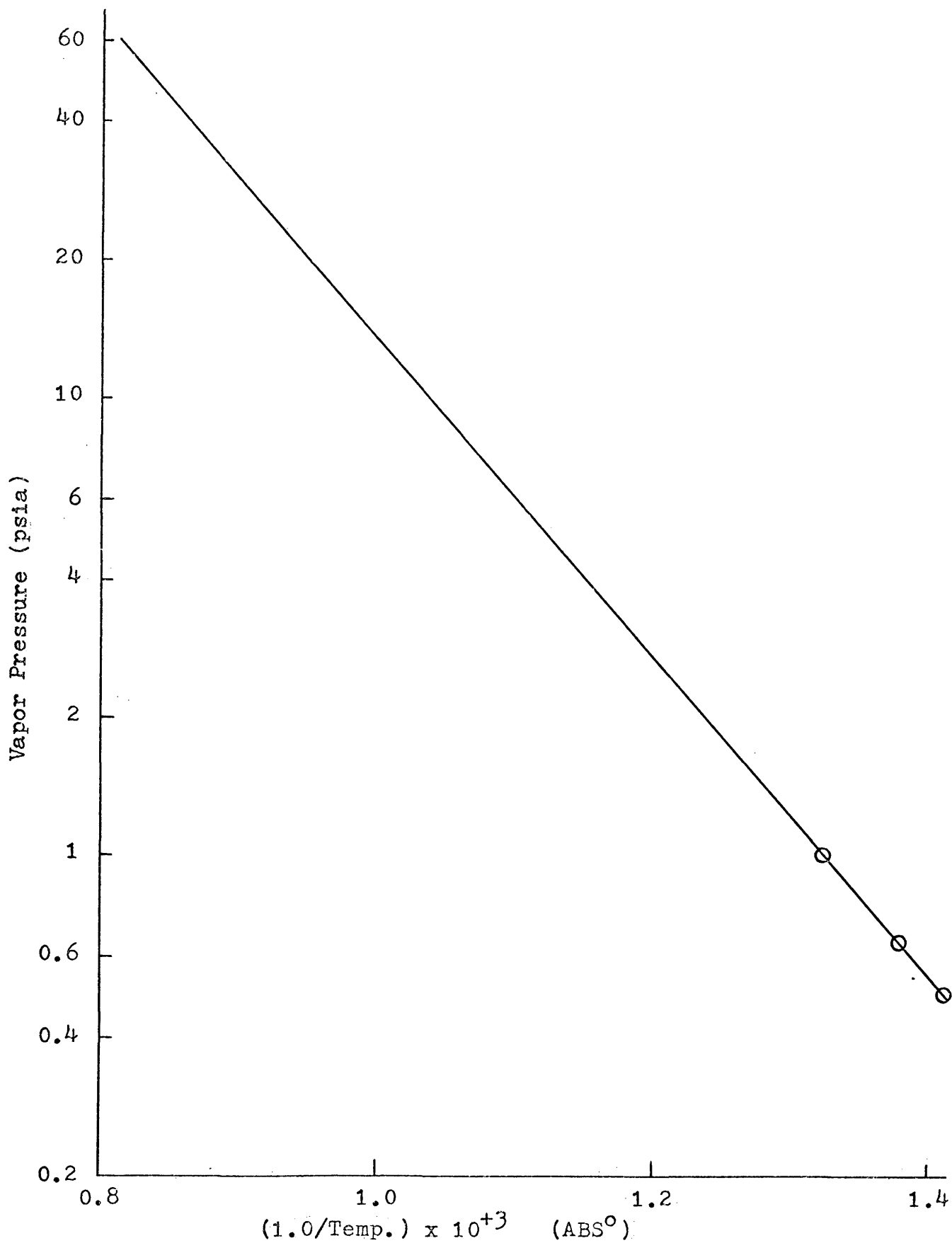


Figure 20: Saturated Vapor Pressure of 2,6-Lutidine

APPENDIX VCalculations for the Phase Diagram of
2,6-Lutidine

The following data were taken from Timmermans (16) for the calculations to determine the phase diagram of the pure component, 2,6-lutidine, that was present in the reactor:

Critical temperature, $T_c = 660^\circ\text{F}$,

Boiling temperature, $T_b = 290^\circ\text{F}$,

Molecular weight, $M = 107.15$ gm/gm-mole.

The critical pressure was calculated from the following equation, and data were taken from Hougen (17):

$$(M/P_c)^{\frac{1}{2}} = 0.34 + \sum \Delta_p$$

The summation of increments from the atomic groups, $\sum \Delta_p$, was determined by the following method for 2,6-lutidine:

$$2(-\text{CH}_3) = 2(0.277) = 0.654$$

$$3(=\overset{\text{I}}{\text{C}}\text{H}) = 3(0.154) = 0.462$$

$$2(=\overset{\text{I}}{\underset{\text{I}}{\text{C}}}) = 2(0.154) = 0.308$$

$$1(=\text{N}-) = 1(0.130) = 0.130$$

$$\sum \Delta_p = 1.554$$

$$(M/P_c)^{\frac{1}{2}} = 0.34 + \sum \Delta_p = 0.34 + 1.554$$

$$(M/P_c)^{\frac{1}{2}} = 1.894$$

$$\text{Solving for } P_c, \quad P_c = M/(1.894)^2 = 107.15/(1.894)^2$$

$$P_c = 30.0 \text{ atm} = 442 \text{ psia}$$

Using the procedure outlined in Nelson (18), the focal pressure and focal temperature were determined in the following manner: with an ASTM slope of 1.0 for 2,6-lutidine at the atmospheric boiling point of 290°F, the focal temperature - critical temperature, $(T_f - T_c) = 63^\circ\text{F}$, and the focal pressure - critical pressure, $(P_f - P_c) = 155 \text{ psia}$.

The focal temperature and pressure were:

$$T_f = 63^\circ\text{F} + T_c = 63^\circ\text{F} + 660^\circ\text{F}$$

$$T_f = 723^\circ\text{F}$$

$$P_f = 155 \text{ psia} + P_c = 155 \text{ psia} + 442 \text{ psia}$$

$$P_f = 597 \text{ psia}$$

Figure 3 was obtained by knowing the focal pressure and temperature, (P_f, T_f) and the boiling point of 2,6-lutidine at 14.7 psia. These two points determined the separation of the liquid and vapor regions when the $\ln P$ was plotted against the Cox temperature. The Cox temperature is a linear scale of the following relation:

$$\text{Cox temperature} = 1.0/(382 + T) \text{ where } T = ^\circ\text{F}.$$

APPENDIX VI

Calculations of the Diffusional Effects
of the System

Two diffusional effects have to be checked to determine whether the reaction was mass transfer controlled from the liquid surface of the reactant to the catalyst pellet or whether there was diffusional effects within the porous catalyst.

The following calculation was made to determine whether the system was controlled by transfer of mass from the liquid reactant to the catalyst pellet. For this transfer the model of steady-state diffusion of 2,6-lutidine through stagnant (nondiffusing) hydrogen gas was assumed. It was assumed that the liquid reactant covered the bottom of the pressure reactor at the measured internal temperature of the pressure reactor. Fick's law was used to obtain the total mass transferred (19):

$$\dot{w}_A = A N_A = \frac{A P D_{AB}}{R T L} \frac{(P_{A1} - P_{A2})}{P_{BM}}$$

where subscript A was 2,6-lutidine and subscript B was hydrogen gas. Subscript 1 and 2 indicate at the liquid surface

and catalyst surface, respectively. It was assumed that the 2,6-lutidine reacts immediately at the catalyst surface; therefore the partial pressure was zero ($P_{A2} = 0$), and at the surface of the reactant the partial pressure was the saturated vapor pressure at the temperature of the system. Appendix IV gives this pressure. P_{BM} was defined as

$$\frac{(P_{B2} - P_{B1})}{\ln (P_{B2}/P_{B1})},$$

the log-mean partial pressure of the nondiffusing component.

The diffusion coefficient, D_{AB} , was determined over the range of the experimental runs. It was assumed that there was a two-component system, gaseous 2,6-lutidine and hydrogen gas. The Chapman-Enskog formula for diffusion coefficients was used as follows:

$$D_{AB} = \frac{0.001858 T^{3/2} ((M_A + M_B)/M_A M_B)^{1/2}}{P \sigma_{AB}^2 \Omega}$$

The following data were taken from Chapter 2 of Satterfield and Sherwood (20) except for the critical temperature of 2,6-lutidine (see Appendix V). The data were as follows:

$$\begin{aligned} P &= 27.2 \text{ atm (400 psig), } 40.8 \text{ atm (600 psig),} \\ &\quad 51.0 \text{ atm (750 psig)} \\ T &= 473^\circ\text{K (400}^\circ\text{F), } 583^\circ\text{K (600}^\circ\text{F), } 673^\circ\text{K (750}^\circ\text{F)} \\ M_A &= 107.15 \text{ gm/gm-mole} \end{aligned}$$

$$M_B = 2.0 \text{ gm/gm-mole}$$

$$T_{Ac} = 350.6^\circ\text{C} = 623.6^\circ\text{K}$$

The collision integral, Ω , was determined from the Lennard-Jones potentials, kT/ϵ_{AB} .

$$\epsilon_B/k = 33.3$$

ϵ_A/k was estimated from the empirical equation,

$$\epsilon_A/k = T_{Ac}/1.30 = 623.6^\circ\text{K}/1.30 = 1/0.00209$$

$$Tk^2/\epsilon_A\epsilon_B = (k^2/\epsilon_A\epsilon_B)^{\frac{1}{2}} T = \frac{(0.00209)^{\frac{1}{2}} T}{33.3} \text{ where}$$

$$\epsilon_{AB} = (\epsilon_A\epsilon_B)^{\frac{1}{2}}$$

$$Tk/\epsilon_{AB} = (0.0698)^{\frac{1}{2}} = 0.263 T$$

$$Tk/\epsilon_{AB} = 124, 154, 170$$

$$\Omega = 0.50, 0.49, 0.47$$

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B)$$

$$\sigma_A = 2.968 \text{ \AA}$$

From an empirical relation,

$$\sigma_B = 1.18 V_b^{1/3}$$

$$9(H) = 9(3.7) = 33.2$$

$$7(C) = 7(14.8) = 103.5$$

$$1(N) = 1(31.2) = 31.2$$

$$\text{-6 membered ring} = -15.0$$

$$V_b = 152.9$$

$$\sigma_A = 1.18 (152.9)^{1/3} = 6.3 \text{ \AA}$$

$$\sigma_{AB} = \frac{1}{2}(6.3 + 2.968) = 4.632 \text{ \AA}$$

$$\sigma_{AB}^2 = 21.4$$

The following equation was obtained for the diffusion coefficient as a function of temperature, T, pressure, P, and the collision intergral, Ω :

$$D_{AB} = 0.001858 T \frac{((107.15 + 2.0)/(107.15)(2.0))^{\frac{1}{2}}}{P (21.4) \Omega}$$

$$D_{AB} = 0.616 \times 10^{-4} T/P\Omega$$

The following values were obtained for the diffusion coefficients:

<u>T (°F)</u>	<u>P (psig)</u>	<u>D_{AB} (cm²/sec)</u>
400	400	0.0456
400	600	0.0303
400	750	0.0243
600	400	0.0652
600	600	0.0434
600	750	0.0348
750	400	0.0840
750	600	0.0559
750	750	0.0448

From the phase diagram of 2,6-lutidine, Figure 3, the two conditions, where the system has a liquid phase, 600°F - 400 psig and 400°F - 600 psig, were used to determine the total mass transferred to the pellets. From the graph in Appendix IV and the above data the following was used:

$$\underline{600^{\circ}\text{F} - 400 \text{ psig}}$$

$$D_{AB} = 0.0652 \text{ cm}^2/\text{sec}$$

$$\text{Sat. Vapor Press.} = 14.0 \text{ psia}$$

$$\underline{400^{\circ}\text{F} - 600 \text{ psig}}$$

$$D_{AB} = 0.0303 \text{ cm}^2/\text{sec}$$

$$\text{Sat. Vapor Press.} = 3.7 \text{ psia}$$

In order to determine the distance the 2,6-lutidine has to be transferred, the catalyst bed was 0.954 cm (3/8") from the bottom of the pressure reactor. 25.0 ml of 2,6-lutidine occupied a depth of 0.33 cm. The following method was used in calculating the total mass transferred.

$$L = 0.954 \text{ cm} - 0.33 \text{ cm} = 0.624 \text{ cm}$$

$$A = \pi R_a^2 = \pi (3.875")^2 (2.54 \text{ cm/in})^2 = 75.8 \text{ cm}^2$$

For vapor pressure = 14.0 psia,

$$P_{BM} = \frac{P_{B2} - P_{B1}}{\ln(P_{B2}/P_{B1})} = \frac{414.7 - 400}{\ln(414/400)} = 412$$

For vapor pressure = 3.7 psia,

$$P_{BM} = \frac{P_{B2} - P_{B1}}{\ln(P_{B2}/P_{B1})} = \frac{614.7 - 611.0}{\ln(614.7/611.7)} = 612$$

$$R = 82.1 \text{ atm cm}^3/\text{gm-mole } ^{\circ}\text{K}$$

$$P = 27.3 \text{ atm (400 psig), } 40.8 \text{ atm (600 psig)}$$

$$T = 583^{\circ}\text{K (600}^{\circ}\text{F), } 473^{\circ}\text{K (400}^{\circ}\text{F)}$$

$$w_A = (APD_{AB}/RTL) (P_{A1}/P_{BM})$$

For 600°F - 400 psig,

$$w_A = \frac{75.8 \text{ cm}^2 \cdot 27.3 \text{ atm} \cdot 0.0652 \text{ cm}^2/\text{sec} \cdot 14 \text{ psia}}{82.1 \text{ atm cm}^3/\text{gm-mole } ^\circ\text{K} \cdot 583^\circ\text{K} \cdot 0.624 \text{ cm} \cdot 412 \text{ psia}}$$

$$w_A = 0.1515 \times 10^{-3} \text{ gm-mole/sec} = 0.544 \text{ gm-mole/hr}$$

For 400°F - 600 psig,

$$w_A = \frac{75.8 \text{ cm}^2 \cdot 40.8 \text{ atm} \cdot 0.0303 \text{ cm}^2/\text{sec} \cdot 3.7 \text{ psia}}{82.1 \text{ atm cm}^3/\text{gm-mole } ^\circ\text{K} \cdot 0.624 \text{ cm} \cdot 473^\circ\text{K} \cdot 612 \text{ psia}}$$

$$w_A = 0.237 \times 10^{-4} \text{ gm-mole/sec} = 0.831 \times 10^{-1} \text{ gm-mole/hr}$$

From the calculations in Appendix VIII, the total moles of 2,6-lutidine in the reactor was 0.213 gm-moles. Since a total of 0.0831 gm-moles/hr would be transferred if diffusion were controlling, 0.1662 gm-moles would be transferred in 2 hours. Therefore in a 2-hour run at 400°F - 600 psig, 0.048 gm-moles would be left. Experimental results for the run indicate that only 0.0106 gm-moles had reacted. It was concluded that this diffusional effect was not controlling.

In order to calculate the diffusional effects within the catalyst, the following method was used. Since the pressure was high and the catalyst pore diameter (see Appendix I for pore diameter) was far greater than 60 Å, the mass was transferred by ordinary diffusion. The effective diffusion coefficient, D_{eff} , was determined from chapter 1 of Satterfield and Sherwood (20). The effective diffusion coefficient could be determined from the following formula:

$$D_{\text{eff}} = D_{\text{AB}} \Theta / \tau \text{ where } \tau = 2.0 \text{ and } \Theta = 0.4 \text{ (void)}$$

$$D_{\text{eff}} = 0.2 D_{\text{AB}}$$

From the previous calculation, the following was obtained:

<u>T (°F)</u>	<u>P (psig)</u>	<u>D_{eff} (cm²/sec)</u>
400	400	0.00912
400	600	0.00606
400	750	0.00286
600	400	0.01304
600	600	0.00868
600	750	0.00696
750	400	0.01680
750	600	0.01118
750	750	0.00898

D_{eff} ranged from 0.00286 to 0.0168 cm²/sec.

Three parameters, Φ , β , δ , had to be calculated to determine whether the diffusion was controlling in the catalyst, and the criteria,

$$\Phi \exp(\delta \beta / \beta + 1) < 1.0$$

were checked.

$$\Phi = \frac{R_s^2}{D_{\text{eff}}} \left(- \frac{1}{V_c} \frac{dn}{dt} \right) \frac{1}{C_s}$$

$$\delta = E/RT$$

$$\beta = \frac{C_S (-\Delta H) D_{\text{eff}}}{\lambda T_S}$$

The following was used to calculate the above parameters at 750°F - 400 psig:

$$\delta = E/RT$$

$$E = 18,780 \text{ cal/gm-mole (taken from experimental data)}$$

$$R = 1.987 \text{ cal/gm-mole } ^\circ\text{K}$$

$$T = 671^\circ\text{K}$$

$$\delta = 14$$

$$\beta = C_S (-\Delta H) D_{\text{eff}} / \lambda T_S$$

$$T_S = 750^\circ\text{F} = 398^\circ\text{C}$$

$$\lambda = 1.12 \times 10^{-3} \text{ cal/sec cm } ^\circ\text{C}$$

$$D_{\text{eff}} = 0.0168 \text{ cm}^2/\text{sec}$$

$-\Delta H$ was calculated from the heats of combustion of 2,6-lutidine to n-heptane. $-\Delta H$ is the heat of reaction.

$$\Delta H = \Delta H_{\text{prod}} - \Delta H_{\text{react}}$$

$$\Delta H = 1151.7 - 968.2 = 183.57 \text{ kcal/gm-mole}$$

$$C_S = 0.213 \text{ gm-moles 2,6-lutidine}/V_R, V_R = 1000 \text{ ml}$$

$$C_S = 2.13 \times 10^{-4} \text{ gm-mole/cm}^3$$

$$\beta = 1.46$$

$$\Phi = R_S^2 / D_{\text{eff}} (1/V_C) (dn/dt) (1/C_S)$$

$$R_S = 3/2 R_C \text{ (radius of catalyst)}$$

$$R_S^2 = 9/4 R_C^2$$

$$R_c = 0.1125 \text{ cm}$$

$$D_{\text{eff}} = 0.0168 \text{ cm}^2/\text{sec}$$

$$V_c = 10 \text{ cm}^3$$

dn/dt for the 750°F - 400 psig run was

$$(0.0623 \text{ gm-moles} - 0.213 \text{ gm-moles})/2\text{hr}$$

$$\frac{dn}{dt} = -2.09 \times 10^{-5} \text{ gm-moles/sec}$$

$$\bar{\Phi} = 0.0001675$$

The criteria, $\bar{\Phi} \exp(\delta \beta / 1.0 + \beta)$, was 0.64, which was less than 1.0, and indicates that the reaction was not diffusion controlled in the catalyst. $\bar{\Phi}$ indicates that it was not diffusional controlled because it was very small, but the reaction was highly endothermic by calculations.

APPENDIX VII

Raw Data and Sample Composition

RUN: 43-649-27

CONDITIONS: 400°F - 400 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	68	250	C3	---
20.0	403	400	C4	---
40.0	405	410	C5	---
60.0	395	405	C6	---
80.0	398	405	C7	0.15
100.0	397	400	C8	0.21
120.0	397	400	2,6-lutidine	99.37
140.0	395	400	Bases	0.27

RUN: 43-649-28

CONDITIONS: 400°F - 400 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	71	250	C3	---
20.0	410	400	C4	---
40.0	400	400	C5	---
60.0	396	400	C6	---
80.0	398	400	C7	0.10
100.0	396	400	C8	0.17
120.0	398	405	2,6-lutidine	96.69
140.0	400	405	Bases	3.04
160.0	400	405		
180.0	400	405		

RUN: 43-649-28 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
200.0	400	405		
220.0	400	405		
240.0	400	400		

RUN: 43-649-29

CONDITIONS: 400°F - 400 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	80	260	C3	---
20.0	405	400	C4	---
40.0	410	405	C5	1.42
60.0	395	400	C6	---
80.0	390	405	C7	0.48
100.0	395	400	C8	---
120.0	396	400	2,6-lutidine	93.15
140.0	402	405	Bases	4.95
160.0	404	405		
180.0	406	405		
200.0	406	405		
220.0	406	410		
240.0	408	408		
260.0	409	408		
280.0	405	408		
300.0	405	408		
320.0	404	400		
340.0	400	400		
360.0	400	405		

RUN: 43-649-49

CONDITIONS: 400°F - 600 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	390	C3	---

RUN: 43-649-49 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	400	600	C4	---
40.0	405	600	C5	---
60.0	395	600	C6	---
80.0	395	595	C7	0.56
100.0	395	595	C8	---
120.0	398	600	2,6-lutidine	98.27
140.0	395	595	Bases	1.17

RUN: 43-649-48

CONDITIONS: 400°F - 600 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	62	400	C3	0.41
20.0	400	600	C4	---
40.0	420	610	C5	---
60.0	402	610	C6	---
80.0	396	600	C7	0.56
100.0	400	610	C8	---
120.0	403	610	2,6-lutidine	95.03
140.0	402	610	Bases	4.00
160.0	400	610		
180.0	402	610		
200.0	406	605		
220.0	403	605		
240.0	400	605		

RUN: 43-649-45

CONDITIONS: 400°F - 600 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	375	C3	---
20.0	400	600	C4	---
40.0	395	600	C5	---

RUN: 43-649-45. (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
60.0	393	600	C6	---
80.0	408	605	C7	1.38
100.0	410	610	C8	---
120.0	408	605	2,6-lutidine	92.32
140.0	403	605	Bases	6.30
160.0	400	610		
180.0	400	605		
200.0	400	605		
220.0	395	600		
240.0	393	605		
260.0	400	605		
280.0	400	600		
300.0	400	600		
320.0	402	605		
340.0	400	605		
360.0	400	600		

RUN: 43-649-36

CONDITIONS: 400°F - 750 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	80	465	C3	---
20.0	410	750	C4	---
40.0	410	750	C5	---
60.0	400	745	C6	---
80.0	410	750	C7	0.24
100.0	400	750	C8	0.47
120.0	395	750	2,6-lutidine	97.60
140.0	390	750	Bases	1.69

RUN: 43-649-38

CONDITIONS: 400°F - 750 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	410	C3	---

RUN: 43-649-38 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	410	755	C4	0.05
40.0	410	740	C5	---
60.0	395	740	C6	---
80.0	400	740	C7	1.04
100.0	400	745	C8	0.33
120.0	400	760	2,6-lutidine	95.07
140.0	400	750	Bases	3.51
160.0	400	750		
180.0	400	750		
200.0	402	745		
220.0	402	750		
240.0	400	755		

RUN: 43-649-39

CONDITIONS: 400°F - 750 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	68	410	C3	---
20.0	405	760	C4	0.40
40.0	390	750	C5	---
60.0	400	750	C6	---
80.0	405	750	C7	0.97
100.0	410	760	C8	0.25
120.0	395	760	2,6-lutidine	93.53
140.0	395	760	Bases	4.85
160.0	392	760		
180.0	392	755		
200.0	396	760		
220.0	395	760		
240.0	398	760		
260.0	400	760		
280.0	400	760		
300.0	400	760		
320.0	400	760		
340.0	400	760		
360.0	400	760		

RUN: 43-649-30

CONDITIONS: 600°F - 400 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	71	205	C3	---
20.0	601	405	C4	---
40.0	606	405	C5	---
60.0	600	405	C6	---
80.0	600	404	C7	1.71
100.0	600	405	C8	0.09
120.0	608	406	2,6-lutidine	95.94
140.0	610	400	Bases	2.26

RUN: 43-649-32

CONDITIONS: 600°F - 400 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	68	200	C3	---
20.0	600	400	C4	---
40.0	590	410	C5	---
60.0	594	410	C6	---
80.0	605	410	C7	3.22
100.0	604	410	C8	0.03
120.0	602	410	2,6-lutidine	90.46
140.0	595	410	Bases	6.29
160.0	594	415		
180.0	594	415		
200.0	594	410		
220.0	598	410		
240.0	596	400		

RUN: 43-649-31

CONDITIONS: 600°F - 400 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	200	C3	---

RUN: 43-649-31 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	610	400	C4	---
40.0	600	400	C5	---
60.0	604	410	C6	---
80.0	605	405	C7	6.39
100.0	606	400	C8	0.21
120.0	606	405	2,6-lutidine	77.28
140.0	606	410	Bases	16.12
160.0	606	405		
180.0	610	408		
200.0	606	410		
220.0	603	410		
240.0	605	410		
260.0	606	410		
280.0	608	410		
300.0	606	410		
320.0	605	410		
340.0	604	405		
360.0	602	405		

RUN: 43-649-50

CONDITIONS: 600°F - 600 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	68	290	C3	---
20.0	600	600	C4	---
40.0	605	605	C5	---
60.0	595	610	C6	---
80.0	595	605	C7	1.64
100.0	596	605	C8	0.30
120.0	598	610	2,6-lutidine	94.78
140.0	595	600	Bases	3.28

RUN: 43-649-47

CONDITIONS: 600°F - 600 psig - 4 hours

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	400	C3	---
20.0	400	600	C4	---
40.0	590	610	C5	---
60.0	600	605	C6	---
80.0	610	605	C7	4.40
100.0	610	605	C8	0.78
120.0	605	605	2,6-lutidine	87.94
140.0	610	605	Bases	7.38
160.0	610	605		
180.0	608	610		
200.0	---	---		
220.0	600	600		
240.0	600	600		

RUN: 43-649-51

CONDITIONS: 600°F - 600 psig - 6 hours

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	70	300	C3	---
20.0	440	450	C4	---
40.0	608	610	C5	---
60.0	604	610	C6	---
80.0	595	610	C7	13.85
100.0	600	610	C8	1.45
120.0	600	605	2,6-lutidine	78.03
140.0	608	600	Bases	6.67
160.0	604	605		
180.0	600	600		
200.0	600	605		
220.0	608	600		
240.0	605	595		
260.0	604	595		
280.0	608	595		
300.0	600	595		
320.0	600	595		
340.0	600	590		
360.0	595	590		

RUN: 43-649-42

CONDITIONS: 600°F - 750 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	350	C3	0.13
20.0	600	700	C4	---
40.0	600	750	C5	---
60.0	595	750	C6	---
80.0	595	745	C7	4.24
100.0	600	750	C8	0.34
120.0	600	750	2,6-lutidine	90.61
140.0	600	750	Bases	4.68

RUN: 43-649-41

CONDITIONS: 600°F - 750 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	70	335	C3	---
20.0	600	740	C4	---
40.0	609	740	C5	---
60.0	595	760	C6	---
80.0	595	760	C7	10.73
100.0	600	760	C8	1.57
120.0	601	760	2,6-lutidine	80.67
140.0	600	760	Bases	7.03
160.0	602	760		
180.0	602	760		
200.0	603	755		
220.0	600	755		
240.0	601	755		

RUN: 43-649-40

CONDITIONS: 600°F - 750 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	355	C3	---

RUN: 43-649-40 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	595	760	C4	---
40.0	595	750	C5	---
60.0	594	750	C6	---
80.0	594	750	C7	14.32
100.0	594	750	C8	0.62
120.0	598	750	2,6-lutidine	76.06
140.0	594	750	Bases	9.00
160.0	595	750		
180.0	595	745		
200.0	595	745		
220.0	596	740		
240.0	595	740		
260.0	594	740		
280.0	594	740		
300.0	596	740		
320.0	598	740		
340.0	596	740		
360.0	593	740		

RUN: 43-649-73

CONDITIONS: 700°F - 350 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	155	C3	---
20.0	660	340	C4	---
40.0	700	350	C5	0.07
60.0	700	355	C6	0.15
80.0	705	355	C7	6.80
100.0	705	355	C8	---
120.0	705	350	2,6-lutidine	88.73
140.0	700	350	Bases	4.25

RUN: 43-649-75

CONDITIONS: 700°F - 350 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	62	140	C ₃	0.08
20.0	625	305	C ₄	0.12
40.0	700	350	C ₅	0.04
60.0	700	360	C ₆	0.16
80.0	700	360	C ₇	22.58
100.0	695	350	C ₈	---
120.0	695	355	2,6-lutidine	67.07
140.0	693	350	Bases	9.95
160.0	695	350		
180.0	700	350		
200.0	705	345		
220.0	700	345		
240.0	700	350		

RUN: 43-649-72

CONDITIONS: 700°F - 400 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	175	C ₃	---
20.0	565	360	C ₄	---
40.0	695	400	C ₅	---
60.0	705	405	C ₆	---
80.0	706	405	C ₇	8.85
100.0	700	400	C ₈	---
120.0	700	400	2,6-lutidine	86.87
140.0	700	400	Bases	4.28

RUN: 43-649-74

CONDITIONS: 700°F - 400 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	170	C ₃	0.20

RUN: 43-649-74 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	645	320	C4	0.22
40.0	695	395	C5	0.20
60.0	704	400	C6	0.54
80.0	700	400	C7	31.96
100.0	700	400	C8	---
120.0	695	395	2,6-lutidine	59.05
140.0	695	395	Bases	8.73
160.0	695	390		
180.0	690	390		
200.0	695	400		
220.0	705	400		
240.0	700	395		

RUN: 43-649-35

CONDITIONS: 750°F - 400 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	140	C3	0.01
20.0	712	400	C4	---
40.0	742	405	C5	0.11
60.0	752	405	C6	0.12
80.0	742	400	C7	13.88
100.0	740	405	C8	0.29
120.0	750	410	2,6-lutidine	72.77
140.0	745	400	Bases	12.82

RUN: 43-649-34

CONDITIONS: 750°F - 400 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	140	C3	---
20.0	680	350	C4	---
40.0	740	390	C5	---
60.0	755	405	C6	0.65

RUN: 43-649-34 (con't)

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
80.0	750	400	C7	29.50
100.0	742	400	C8	1.30
120.0	744	395	2,6-lutidine	49.65
140.0	748	395	Bases	18.90
160.0	750	395		
180.0	756	390		
200.0	750	390		
220.0	750	390		
240.0	750	390		

RUN: 43-649-33

CONDITIONS: 750°F - 400 psig - 6 hours

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	62	175	C3	0.17
20.0	665	400	C4	0.19
40.0	720	400	C5	0.16
60.0	760	420	C6	0.77
80.0	740	400	C7	39.90
100.0	740	400	C8	1.70
120.0	742	405	2,6-lutidine	36.32
140.0	748	400	Bases	20.79
160.0	750	400		
180.0	755	405		
200.0	751	400		
220.0	748	400		
240.0	747	400		
260.0	748	395		
280.0	750	395		
300.0	751	395		
320.0	753	395		
340.0	754	392		
360.0	750	395		

RUN: 43-649-67

CONDITIONS: 750°F - 600 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	260	C3	---
20.0	545	460	C4	0.67
40.0	755	600	C5	0.62
60.0	750	600	C6	1.36
80.0	755	605	C7	21.02
100.0	750	600	C8	1.41
120.0	754	604	2,6-lutidine	42.94
140.0	745	600	Bases	31.88

RUN: 43-649-53

CONDITIONS: 750°F - 600 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	280	C3	---
20.0	675	550	C4	0.41
40.0	750	600	C5	0.19
60.0	690	590	C6	0.75
80.0	730	600	C7	73.10
100.0	740	600	C8	0.21
120.0	745	600	2,6-lutidine	12.11
140.0	745	600	Bases	13.23
160.0	745	600		
180.0	740	600		
200.0	750	600		
220.0	750	595		
240.0	750	595		

RUN: 43-649-76

CONDITIONS: 750°F - 600 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	260	C3	---

RUN: 43-649-76 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
20.0	710	600	C4	0.36
40.0	750	600	C5	0.20
60.0	745	600	C6	0.60
80.0	740	610	C7	70.28
100.0	745	600	C8	0.15
120.0	750	600	2,6-lutidine	20.38
140.0	750	610	Bases	8.03
160.0	750	615		
180.0	750	600		
200.0	755	600		
220.0	750	600		
240.0	755	595		

RUN: 43-649-55

CONDITIONS: 750°F - 600 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	260	C3	1.39
20.0	595	500	C4	1.63
40.0	755	600	C5	0.89
60.0	755	605	C6	3.52
80.0	695	580	C7	77.58
100.0	740	600	C8	0.64
120.0	740	600	2,6-lutidine	7.20
140.0	750	600	Bases	7.15
160.0	750	600		
180.0	748	600		
200.0	745	590		
220.0	750	600		
240.0	748	600		
260.0	750	600		
280.0	755	600		
300.0	750	590		
320.0	745	590		
340.0	750	590		
360.0	745	590		

RUN: 43-649-46

CONDITIONS: 750°F - 750 psig - 2 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	410	C3	0.22
20.0	700	740	C4	0.72
40.0	750	750	C5	0.40
60.0	690	690	C6	0.67
80.0	740	700	C7	55.56
100.0	750	740	C8	0.18
120.0	750	735	2,6-lutidine	29.28
140.0	748	750	Bases	12.97

RUN: 43-649-44

CONDITIONS: 750°F - 750 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	70	320	C3	1.30
20.0	700	680	C4	0.98
40.0	749	755	C5	0.52
60.0	745	750	C6	0.39
80.0	729	740	C7	74.15
100.0	740	700	C8	0.10
120.0	745	745	2,6-lutidine	5.39
140.0	750	745	Bases	17.27
160.0	750	745		
180.0	745	750		
200.0	750	755		
220.0	750	740		
240.0	740	745		

RUN: 43-649-78

CONDITIONS: 750°F - 750 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	68	320	C3	0.28
20.0	700	680	C4	0.68

RUN: 43-649-78 (con't)

CONDITIONS: 750°F - 750 psig - 4 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
40.0	750	750	C ₅	0.62
60.0	750	750	C ₆	0.38
80.0	745	755	C ₇	70.63
100.0	746	750	C ₈	0.10
120.0	750	750	2,6-lutidine	9.64
140.0	755	745	Bases	17.57
160.0	750	745		
180.0	750	745		
200.0	750	740		
220.0	745	750		
240.0	745	750		

RUN: 43-649-52

CONDITIONS: 750°F - 750 psig - 6 hours

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	70	260	C ₃	0.85
20.0	540	668	C ₄	1.05
40.0	750	740	C ₅	1.03
60.0	700	690	C ₆	1.27
80.0	745	745	C ₇	74.75
100.0	740	740	C ₈	0.73
120.0	740	740	2,6-lutidine	3.27
140.0	730	730	Bases	17.05
160.0	750	750		
180.0	750	750		
200.0	740	740		
220.0	750	750		
240.0	760	760		
260.0	755	755		
280.0	745	745		
300.0	745	745		
320.0	740	740		
340.0	745	745		
360.0	745	745		

APPENDIX VIIICalculations to Determine the Concentration
of 2,6-Lutidine

The $\ln (C_t/C_o)$ versus reaction time was plotted to determine the reaction rate constant. The weight percent of each group was determined from the raw data. The following calculation was how the concentrations were obtained:

$$\text{Concentration, } C_t = n_t/V_R, \text{ gm-moles/cm}^3$$

$$V_R = \text{volume of pressure reactor} = 1000 \text{ cm}^3$$

$$n_t = \text{gm-moles of 2,6-lutidine at time, } t$$

$$C_t/C_o = (n_t/V_R) (V_R/n_o), \text{ volume of reactor constant}$$

$$C_t/C_o = n_t/n_o$$

$$n_t = 25.0 \text{ cm}^3 (\text{Sp. Gr.}) (\text{wt. fract.})/M_A$$

$$n_o = 0.213 \text{ gm-moles}$$

$$C_t/C_o = (\text{wt. fract.})$$

Therefore to obtain C_t/C_o , the ratio of the weights was taken.

APPENDIX IX

Analysis of Variance and Replicate Runs

The following was the raw data and compositions taken experimentally for the replicate runs.

CONDITIONS: 750°F - 600 psig - 4 hr

RUN: 43-649-53

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	280	C ₃	---
20.0	675	550	C ₄	0.41
40.0	750	600	C ₅	0.19
60.0	690	590	C ₆	0.75
80.0	730	600	C ₇	73.10
100.0	740	600	C ₈	0.21
120.0	745	600	2,6-lutidine	12.11
140.0	745	600	Bases	13.23
160.0	740	600		
180.0	750	600		
200.0	750	595		
220.0	750	595		
240.0	---	---		

RUN: 43-649-64

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	50	260	C ₃	0.04
20.0	710	600	C ₄	0.18
40.0	755	610	C ₅	---
60.0	750	605	C ₆	0.05
80.0	750	605	C ₇	72.58

RUN: 43-649-64 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
100.0	710	590	C ₈	5.35
120.0	740	600	2,6-lutidine	14.56
140.0	750	600	Bases	7.25
160.0	750	600		
180.0	750	600		
200.0	743	595		
220.0	745	595		
240.0	740	595		

RUN: 43-649-61

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	63	250	C ₃	0.04
20.0	485	405	C ₄	0.39
40.0	750	600	C ₅	0.21
60.0	748	600	C ₆	0.98
80.0	720	580	C ₇	75.76
100.0	745	595	C ₈	6.06
120.0	740	600	2,6-lutidine	10.16
140.0	750	600	Bases	6.41
160.0	750	600		
180.0	750	600		
200.0	750	600		
220.0	750	600		
240.0	750	600		

CONDITIONS: 600°F - 600 psig - 4 hr

RUN: 43-649-56

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	65	280	C ₃	---
20.0	530	480	C ₄	---
40.0	600	590	C ₅	---
60.0	600	600	C ₆	---
80.0	600	590	C ₇	3.04
100.0	600	600	C ₈	0.51
120.0	600	600	2,6-lutidine	90.73
140.0	600	600	Bases	5.72

RUN: 43-649-56 (con't)

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
160.0	600	600		
180.0	600	600		
200.0	600	600		
220.0	600	600		
240.0	600	600		

RUN: 43-649-59

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	280	C3	---
20.0	465	440	C4	---
40.0	600	600	C5	---
60.0	595	600	C6	---
80.0	600	600	C7	5.03
100.0	600	600	C8	0.80
120.0	602	600	2,6-lutidine	86.73
140.0	601	600	Bases	7.44
160.0	600	600		
180.0	600	600		
200.0	600	600		
220.0	598	600		
240.0	595	600		

RUN: 43-649-58

<u>TIME</u> (min)	<u>TEMP</u> (°F)	<u>PRESS</u> (psig)	<u>COMPOUND</u>	<u>WT. %</u>
0.0	70	285	C3	---
20.0	580	590	C4	---
40.0	590	600	C5	---
60.0	595	600	C6	---
80.0	605	600	C7	3.20
100.0	600	595	C8	0.81
120.0	600	595	2,6-lutidine	88.19
140.0	600	600	Bases	7.79
160.0	600	600		
180.0	600	600		
200.0	602	600		
220.0	600	600		
240.0	595	600		

RUN: 43-649-57

<u>TIME</u> <u>(min)</u>	<u>TEMP</u> <u>(°F)</u>	<u>PRESS</u> <u>(psig)</u>	<u>COMPOUND</u>	<u>WT. %</u>
0.0	60	280	C3	---
20.0	465	440	C4	---
40.0	600	600	C5	---
60.0	595	600	C6	---
80.0	600	600	C7	6.33
100.0	600	600	C8	0.60
120.0	602	600	2,6-lutidine	86.12
140.0	601	600	Bases	6.95
160.0	600	600		
180.0	600	600		
200.0	600	600		
220.0	598	590		
240.0	595	590		

The following formulas were used to determine the analysis of variance and the "total worth" of the products formed. The standard deviation, s , was determined, and this was assumed to be σ_k , the variance in the compound determination. The compound groups, $C_3, C_4, C_5, C_6, C_7, C_8$, 2,6-lutidine, and bases were numbered 1 through 8, respectively. The mean of each of these groups were determined with a confidence interval at 95-percent probability assuming independent observations. The t-test was used to determine all variances (standard deviation) since the variation, σ_k , was not known. The variance-covariance matrix was determined for the set of replicate runs.

The observed weight percent was denoted by Y_{ki} . The k or k' indicates which compound group, and the i indicates the individual observation.

$$\text{Mean} = \bar{Y}_k = \sum Y_{ki}/n \text{ for } k = 1, 2, \dots, 8$$

$$\text{Standard deviation} = s_k = \left(\sum (Y_{ki} - \bar{Y}_k)^2 / n - 1 \right)^{\frac{1}{2}}$$

The "total worth" was

$$W = \sum_1^8 C_k \bar{Y}_k$$

where C_k was the profit realized per weight percent of compound k , and \bar{Y}_k was the mean of the k^{th} group. The variance of the "total worth" was given by (21)

$$s_w^2 = \text{var } w = \sum C_k^2 \sigma_k^2 + 2 \sum_{k \neq k'} C_k C_{k'} \sigma_k \sigma_{k'} \rho_{kk'}$$

where the first term was the variance, the second term was the covariance, and σ_k or $\sigma_{k'}$ was estimated by the standard deviation, s_k .

The covariance term can be express in the following equations:

$$2 \sum_{k \neq k'} \sum C_k C_{k'} \sigma_k \sigma_{k'} \rho_{kk'}$$

$$2 \sum_{k \neq k'} \sum C_{k'} C_k \rho_{kk'} \sigma_k \sigma_{k'}$$

where $\rho_{kk'} \sigma_k \sigma_{k'} = \sigma_k \sigma_{k'} r_{kk'}$

$$r_{kk'} = \frac{\sum (Y_{ki} - \bar{Y}_k)(Y_{k'i} - \bar{Y}_{k'})}{\left\{ \left[\sum (Y_{ki} - \bar{Y}_k)^2 \right] \left[\sum (Y_{k'i} - \bar{Y}_{k'})^2 \right] \right\}^{\frac{1}{2}}}$$

$$r'_{kk'} = \rho_{kk'} \sigma_k \sigma_{k'} = \sum (Y_{ki} - \bar{Y}_k)(Y_{k'i} - \bar{Y}_{k'})$$

$$r'_{kk'} = \rho_{kk'} \sigma_k \sigma_{k'} = n \sum Y_{ki} Y_{k'i} - (\sum Y_{ki})(\sum Y_{k'i})$$

therefore

$$2 \sum_{k \neq k'} \sum \sum_{i=1}^n C_k C_{k'} (n \sum Y_{ki} Y_{k'i} - (\sum Y_{ki})(\sum Y_{k'i}))$$

was the covariance term.

The variance-covariance matrix was a symmetric matrix with the variance terms along the diagonal and the covariance terms symmetrically placed on either side of the diagonal.

Data for 750°F - 600 psig - 4 hr

k	#53	RUN Y _{ki} #64	#61	\bar{Y}_k	$\sum Y_{ki}$	s _k	Confidence interval 95% probability
1	---	0.04	0.04	0.027	0.08	0.0231	+ 0.0578
2	0.41	0.18	0.39	0.327	0.98	0.162	+ 0.405
3	0.19	---	0.21	0.133	0.40	0.116	+ 0.290
4	0.75	0.05	0.98	0.593	1.78	0.485	+ 1.214
5	73.10	72.58	75.76	73.813	221.44	1.705	+ 4.26
6	0.21	5.35	6.06	3.873	11.62	3.19	+ 7.98
7	12.11	14.56	10.16	12.276	36.83	2.205	+ 5.51
8	13.23	7.25	6.41	8.963	26.89	3.12	+ 9.30

Data for 600°F - 600 psig - 4 hr

k	#56	RUN Y _{ki} #59	#57	\bar{Y}_k	$\sum Y_{ki}$	s _k	Confidence interval 95% probability
5	3.04	5.03	6.33	4.40	17.60	1.565	+ 2.35
6	0.51	0.80	0.60	0.68	2.72	0.149	+ 0.222
7	90.73	86.73	86.12	87.942	351.77	2.05	+ 3.08
8	5.72	7.44	6.95	6.975	27.90	0.904	+ 1.35

A sample calculation of r'_{kk} was as follows for the 600°F - 600 psig - 4 hr:

$$r'_{56} = n \sum Y_{5i} Y_{6i} - \sum Y_{5i} \sum Y_{6i},$$

$$n = 4$$

$$\sum Y_{5i} = 17.60$$

$$\sum Y_{6i} = 2.72$$

$$\sum Y_{5i} \sum Y_{6i} = 47.872$$

$$n \sum Y_{5i} Y_{6i} = 46.7296$$

$$r'_{56} = -0.1424$$

The two following matrix's were obtained for 600°F - 600 psig - 4 hr, and 750°F - 600 psig - 4 hr, respectively.

$$\sigma_k \sigma_{k'} \rho_{k'k} = \begin{pmatrix} 2.454 & & & \\ -0.1424 & 0.0222 & & \\ -31.384 & -1.7652 & 4.1931 & \\ 3.8932 & 1.5084 & -15.2598 & 0.8187 \end{pmatrix}$$

For the 600°F - 600 psig - 4 hr run using the matrix and the developed equations assuming C_k equals \$1 per weight percent, the value of σ_w was \$8.88. With the same assumptions the run at 750°F - 600 psig - 4 hr was \$12.68.

This would give the following interval 70-percent of the time for each run of the expected profit.

\$100 ± \$8.88 for 600°F

\$100 ± \$12.68 for 750°F

APPENDIX XData Obtained from the Polynomial
Fitting Figures 7 through 19

Figures 7 through 19 were obtained by a least-squares fit of a 1st order polynomial with side conditions or constraints. The following was the sample calculation for this. Some data were obtained from computer out-put.

For Figures 7 through 17 the following model was used since the plot had to pass through $\ln(C_t/C_0)$ at reaction time = 0.

$$y_i = B x_i$$

$$\epsilon = \sum (y_i - Bx_i)^2$$

$$\partial \epsilon / \partial B = -2 \sum x_i (y_i - Bx_i) = 0$$

Solving for \hat{B} ,

$$\hat{B} = \sum x_i y_i / \sum x_i^2$$

Therefore an estimate of the slope was

$$\hat{B} = \sum x_i y_i / \sum x_i^2 \text{ where}$$

x_i = reaction time, t, hr

y_i = $\ln(C_t/C_0)$

A typical example calculation would be for 400°F - 400 psig and was as follows:

$x_i = t$	C_t/C_o	$\ln (C_t/C_o) = y_i$	$\sum x_i^2$	$\sum x_i y_i$
0	1.0000	0.0000	0	0.0000
2	0.9937	-0.00632	4	-0.01264
4	0.9669	-0.03366	16	-0.13464
6	0.9315	-0.07092	<u>36</u>	<u>-.42532</u>
			56	-0.57280

$$\hat{B} = \sum x_i y_i / \sum x_i^2 = -0.01023$$

The following table were the results obtained for \hat{B} . \hat{B} was the estimate of the reaction rate constant, k (hr⁻¹).

<u>CONDITION</u>	<u>\hat{B}</u>
400°F - 400 psig	-0.01023
400°F - 600 psig	-0.0128
400°F - 750 psig	-0.0116
600°F - 400 psig	-0.0363
600°F - 600 psig	-0.0377
600°F - 750 psig	-0.0482
700°F - 350 psig	-0.0924
700°F - 400 psig	-0.119
750°F - 400 psig	-0.170
750°F - 600 psig	-0.448
750°F - 750 psig	-0.611

Figures 18 and 19 were fitted to the model,

$$y_i = Bx_i + A.$$

The computer was used to calculate B and A. The following were the results obtained for Figure 18. The results for Figure 19 are given in Appendix XI. In the physical model,

the following symbols correspond to the linear equation:

$$\ln k = y_i, \ln k_o = \hat{A}, 1/T = x_i, \text{ and } \hat{B} = -E/R.$$

Press (psig)	B = -E/R	E <u>kcal</u> <u>gm-mole</u>	A = ln k _o	k _o (hr ⁻¹)
750	-11.0835	22.02	8.17137	6.59 x 10 ¹⁸
600	-9.8222	19.52	6.78613	4.25 x 10 ¹⁵
400	-9.703	19.28	6.253	2.51 x 10 ¹⁴
overall	-9.4527	18.78	6.30714	3.35 x 10 ¹⁴

APPENDIX XI

Data on Catalyst Activity

RUN	HOURS CATALYST (hr) USED			COMPOUNDS (WT. %)		
	BEGINNING	END	AVERAGE	2,6-LUTIDINE	TOTAL HYDROCARBON	
43-649-46	6	10	8	12.11	74.66	
43-649-64	8	12	10	14.56	78.20	
43-649-61	0	4	2	10.16	83.44	

LEAST-SQUARES FIT

<u>COMPOUND</u>	<u>INTERCEPT</u>	<u>SLOPE</u>
2,6-lutidine	12.69	-0.1145
total hydrocarbon	81.84	-0.8397

RUN	HOURS CATALYST (hr) USED			COMPOUNDS (WT. %)		
	BEGINNING	END	AVERAGE	2,6-LUTIDINE	TOTAL HYDROCARBON	
43-649-56	0	4	2	90.73	3.55	
43-649-59	12	16	14	86.73	5.83	
43-649-58	8	12	10	88.19	4.01	
43-649-57	4	8	6	86.12	6.90	

LEAST-SQUARES FIT

<u>COMPOUND</u>	<u>INTERCEPT</u>	<u>SLOPE</u>
2,6-lutidine	89.05	-0.4278
total hydrocarbon	7.79	+0.4974

NOMENCLATURE

A	Area for mass diffusion	cm ²
C _k	Profit per weight percent k th group	\$/wt. percent
C ₀	Initial concentration	gm-mole/cm ³
C _s	Concentration at outside of catalyst	gm-mole/cm ³
C _t	Concentration at any time, t	gm-mole/cm ³
D	Diffusion coefficient	cm ² /sec
D _{eff}	Effective diffusion coefficient	cm ² /sec
dn/dt	Rate of reaction	gm-mole/sec
E	Energy of activation	kcal/gm-mole
ΔH	Enthalpy change on reaction	cal/gm-mole
k	Reaction rate constant	hr ⁻¹
k ₀	Reaction rate pre-exponential	hr ⁻¹
L	Length	cm
M	Molecular weight	gm/gm-mole
N	Diffusion flux	gm-mole/cm ² -hr
n	Order of reaction, number of observations	
P	Pressure	psia, mm Hg
P _c	Critical pressure	atm
P _f	Focal pressure	psia

R	Gas law constant	atm-cm ³ /gm-mole ^{°K} , kcal/gm-mole ^{°K}
R _s	Radius of catalyst	cm
S _k	Standard deviation of k th -group	
T	Temperature	ABS [°]
T _b	Boiling temperature at atmospheric conditions	
T _c	Critical temperature	
T _f	Focal temperature	°F
T _s	Surface temperature of catalyst	°K
t	Reaction time	hr
V _b	Critical volume	
V _c	Catalyst particle volume	cm ³
V _R	Volume of reactor	cm ³
W	"total worth" or profit	\$
Y _{ki}	Weight percent of the i th -observation in k th -group	
\bar{Y}_k	Mean weight percent of k th -group	
β	Heat generation function = $C_s(\Delta H)D_{eff}/T_s$	
δ	Exponent in Arrhenius reaction rate expression = E/RT	
ϵ	Lennard-Jones force constant	
η	Effectiveness factor, the ratio of the actual rate of reaction in a porous catalyst to that which would occur if the pellet were exposed to the same temperature and concentration existing at the surface of the pellet.	
Θ	Porosity (void fraction)	

λ	Thermal conductivity of porous structure	cal/sec-cm ^o C
$\rho_{kk'}$	Correlation coefficient	
σ_A	Atomic radius	Å
σ_k	(Variance) ^{1/2} of the k th -group	
γ	Empirical factor to correct for "tortousity"	
Φ	Dimensionless modulus containing only observable or predictable quantities	
Ω	Collision integral	
ω	Total mass transferred	gm-mole/sec

SUBSCRIPTS

A	2,6-Lutidine
B	Hydrogen gas
1	Position
2	Position

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