

KINETICS OF THE CATALYTIC HYDROGENATION OF
N-HEPTANAL WITH COPPER-CHROMIUM OXIDE CATALYST

by

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ABSTRACT

The kinetics of the catalytic hydrogenation of n-heptanal to n-heptyl alcohol at high temperatures, 250°F to 350°F, and high pressures, 800 psig to 1000 psig, were studied in a stirred tank reactor. Kinetic data on the hydrogenation of aldehydes above butyraldehyde are nonexistent. The availability of n-heptanal as a natural by-product of castor oil prompted its choice for this study.

The n-heptanal and copper chromite catalyst were charged to the reactor prior to heating, and upon reaching the reaction temperature, high pressure hydrogen was injected. Sampling at specified time intervals was accomplished through a convenient sample line which extended directly into the liquid phase. Chromatography was applied to analyze the liquid samples.

Eight experimental runs were made using specific combinations of the four important reaction variables in each run. These variables were: temperature, pressure, catalyst size, and catalyst to reactant weight ratio. The reaction rate was found to increase for the following change in variables: increased temperature, decreased catalyst size, and increased catalyst to reactant weight ratio. The change in pressure of the system had no observable effect upon the reaction rate.

The reaction was found to be zero order with respect to the aldehyde for high concentrations of the n-heptanal, and first order with respect to the aldehyde at high alcohol concentrations.

The slowest or rate controlling step for the zero order portion of the reaction was thought to be the surface reaction between the adsorbed aldehyde and adsorbed hydrogen. When the reaction changed from zero order to first order, three possibilities arose. The adsorption of the heptaldehyde could control, the diffusion of the heptaldehyde to the catalyst surface could control, or the diffusion of the n-heptyl alcohol to the bulk liquid phase could control. It can not be clearly discerned from the data which of these steps is rate controlling at high conversions.

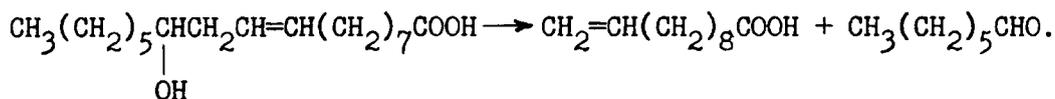
Copper chromite was found to be a very effective catalyst in that 99.9 percent conversion of the n-heptanal was obtained. Only slight reduction of the catalyst took place thereby verifying the ability of the incorporated barium oxide as a promoter and stabilizer.

I. INTRODUCTION

Agricultural by-products are finding numerous new uses in the chemical industries each year, yet there exists a large void in the technology of the chemical processing of these products.

A particular field of interest lies in the production of the alcohols of these by-products through hydrogenation reactions. Hydrogenation reactions can be used to produce both saturated and unsaturated alcohols from the corresponding acids, aldehydes, and esters of the alcohols depending upon the catalyst and conditions which are employed.

In particular, heptaldehyde was chosen for study since it is the most readily available of the higher carbon aldehydes. After castor oil has been extracted from the castor bean, one of the major constituents remaining is ricinoleic acid. Upon destructive distillation of the ricinoleic acid, both 10-hen-decenoic acid and heptaldehyde remain (34). The reaction that occurs is:



The reduction of the aldehyde to the corresponding

alcohol does not necessarily have to be accomplished by gaseous hydrogenation. In fact, earlier studies in the production of n-heptyl alcohol from heptaldehyde were conducted in several different ways. Probably the earliest reaction was that of Bouis and Carlet in 1862, in which heptaldehyde was reduced to n-heptyl alcohol by using zinc dust in the presence of acetic acid (4). Several years later Schrolemmer employed a similar technique in that he used acetic acid as a solvent, but he substituted a sodium amalgam for the zinc dust as a reducing agent (36). The Bouveault-Blanc reduction technique of sodium metal in ethanol was used about this time also (17). A variation of the three methods already mentioned appeared later when Levene and Taylor in 1918, reduced heptaldehyde to n-heptyl alcohol in a mixture of sodium in toluene and acetic acid (24).

After these methods had been used successfully, little was done until the advent of platinum and palladium catalysts. In 1924, Carothers and Adams used a platinum oxide catalyst in a dilute ferric salt solution with the heptaldehyde and obtained 70 percent to 80 percent yields of n-heptyl alcohol (6).

About 1930, a large amount of hydrogenation research had begun to take place at the University of Wisconsin under the direction of Dr. Homer Adkins. His principal interest was in the field of nickel and copper-chromium oxide catalysts, although the work was not strictly limited to these two catalysts (1). Heptaldehyde was reduced in a 95 percent yield to n-heptyl alcohol

using a Raney nickel catalyst, a temperature of 150°C, a pressure of three atmospheres, and a catalyst ratio of six grams catalyst per 285 grams of heptaldehyde with a reaction time of four hours.

The ability of nickel to catalyze hydrogenation reactions was well established by now, yet the Raney or Kieselghur nickel catalyst could be easily poisoned by certain trace impurities of sulfur or halogens (2). The copper-chromium oxide catalyst was found to be less sensitive than nickel to these poisoning agents, and it had the additional advantage of not requiring special preparation before usage as was the case with the nickel. However, much higher pressures of the order of magnitude of 50 to 300 atmospheres are necessary when working with copper-chromium oxide (19).

Another improvement was made on the copper-chromium oxide catalyst in 1932, when Adkins along with several associates found that the addition of barium, calcium and magnesium stabilized the catalyst against reduction, and consequent deactivation, while apparently enhancing its activity (8).

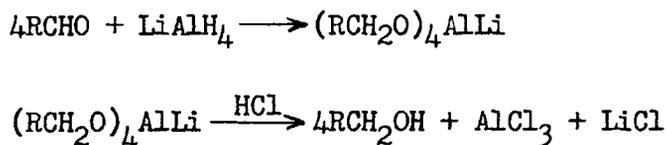
Apparently the interest in using the copper-chromium oxide catalyst to produce n-heptyl alcohol ceased for some time after Adkins' initial work, for the next attempt to produce the alcohol was reported in 1939. Several Russian chemists found that they could obtain a 98 percent yield of n-heptyl alcohol by reacting 100 grams of heptaldehyde in 300 milliliters of 96

percent ethanol with 100 grams of pyrophoric nickel at 55°C and one atmosphere pressure (5).

The next year a report appeared in a French journal which stated that an equimolar solution of n-heptyl alcohol and 2-pentyl-1-nonanal was obtained by reacting two moles of heptaldehyde in the presence of 49 grams of nickel catalyst at temperatures ranging from 25°C to 100°C (31). This article also stated that the hydrogenation was accompanied by aldolization and crotonization. This was the first mention of side reactions.

In 1942, two Chinese chemists reported that n-hexane and n-heptyl alcohol were obtained when heptaldehyde was hydrogenated at 250°C, one atmosphere pressure, and with a Kieselghur nickel catalyst being employed (43). This reaction was carried out completely in the vapor phase and small traces of carbon monoxide and water were found in the product mixture.

The next decade brought about the advent of the metal hydride catalysts such as LiAlH_4 and NaBH_4 . The reduction of heptaldehyde with LiAlH_4 in a hydrochloric acid atmosphere would be a consecutive reaction following these steps (17):



where $\text{R} = \text{CH}_3-(\text{CH}_2)_5-$.

The metal alkoxides could also be used for the direct reduction of the heptaldehyde.

Several Russian publications appeared in 1956 dealing with the hydrogenation of heptaldehyde. One publication stated that the barium and calcium stabilized copper chromite catalyst had facilitated 95 percent to 100 percent conversion to n-heptanol at temperatures ranging from 160°C to 300°C, and pressures from 1 to 200 atmospheres (22). This work was conducted exclusively in the vapor phase in a flow reactor. A second publication in 1956 stated that nickel sulfide and tungsten sulfide on activated alumina had been employed as catalysts in the hydrogenation reaction (25). However, a hydrogen to aldehyde ratio of 1000:1 was used along with a pressure of 300 atmospheres and a temperature of 230°C to obtain a 90 percent yield. Similar results were obtained in a few exploratory tests using an aluminum-cobalt-molybdenum catalyst. Groggins has stated that the sulfide catalysts used in this type of work are advantageous only when the reaction mixture contains sulfur poisons (19). The latest Russian article stated that the hydrogenation ability of copper chromite is dependent upon the crystal lattice constants and the filling of the d shell (40).

With this background in mind, a research project was undertaken for the specific purpose of obtaining the specific reaction rate constants, the order of the reaction, and activation energies for the reaction of heptaldehyde and hydrogen at temperatures of 250°F to 350°F, pressures of 800 psi to 1000 psi, using barium stabilized copper-chromium oxide catalyst.

Industrially promising chemical reactions are often thoroughly studied in bench scale reactors to explore the useful ranges of pressures, temperatures, and catalyst ratios, or to evaluate other reactor variables.

In order to simplify this study the hydrogen was kept in large excess so that all data was reported on the basis of aldehyde concentration only. In other words, this was a pseudo-reaction study.

The objective of this research also included a determination of the rate controlling step in this heterogeneous reaction. Nine important steps can control the reaction rate; therefore, the reaction variables such as temperature, pressure, catalyst size, and catalyst to reactant ratio were varied in such a manner as to gain the proper insight into the rate controlling step.

II. APPARATUS

A. High Pressure Reactor

All of the hydrogenation reactions were carried out in a Series 4500 One-liter Parr Instrument Company high pressure reactor, as illustrated in Figure 3.

The reactor was mounted inside of a steel circular encasement, 10 inches in diameter with a $4\frac{1}{2}$ -inch circular hole in which the reactor was placed. Inside the encasement were heating coils, and the power input to these coils was controlled by a Variac. Both the Variac and the reactor were mounted on a $\frac{1}{4}$ -inch steel base plate which facilitated the moving of the entire system if so desired.

The reactor was constructed of 316 stainless steel, using Teflon gaskets to seal the reactor head and the reactor proper. Two semi-circular clamps were bolted securely into place about the reactor head, and a steel band encircled the two clamps. Extending down into the reactor were the gas injection line and sampling line, the 6-bladed $2\frac{1}{4}$ -inch mixing impeller, and the cooling coils.

Extending from the top surface of the reactor head were six objects. First was the pressure gauge which had a range of 0 to 2000 psi, and was divided into 20 psi increments. The pressure could be read to the nearest 5 psi. Second were the needle

valves which controlled the gas input and sampling lines. Two separate valves controlled these operations independently. Third was the gas outlet line which was controlled by another needle valve. The fourth item was the safety blow-out line which was connected directly to the outside vent line. Inside of this line was a special silver rupture disc, $\frac{1}{2}$ -inch in diameter and 0.010 inches thick, which was rated to rupture at a pressure of 1800 psi. The reactor was tested at the factory up to 3000 psi, but was never operated above 1025 psi, thus leaving a sufficient safety margin. The fifth item was the stirrer shaft which was topped with a $5\frac{1}{2}$ -inch pulley. A "V-belt" connected the pulley to a 1/20 horsepower motor which drove the stirrer at a constant speed. The last item was a thermometer which had a range of 0°C to 500°C, and which could be read accurately to the nearest five degrees.

All electrical connections were explosion-proof.

B. Flow System

Two separate $\frac{1}{4}$ -inch stainless steel tubing lines led from the nitrogen and hydrogen gas bottles to a joining manifold. A Hoke valve was placed in the line leading from the nitrogen bottle so that the high hydrogen pressure could be kept from contacting the nitrogen pressure regulator. A $\frac{1}{4}$ -inch stainless steel tubing line led from the manifold to the gas inlet needle valve.

On the outlet side, $\frac{3}{8}$ -inch stainless steel tubing led from the outlet needle valve to a "T". From the "T" two routes could be followed by the gas. The first route went through

another Hoke valve and then directly to the vent line. The second route went to a Hoke valve and then through a Brooks hydrogen flowmeter and eventually out through the vent line. The operating procedure determined which of the two routes was traversed by the gas.

The vent line was directed out of the laboratory and emerged about 12 feet above the ground level into the open atmosphere.

The safety blow-out line was $3/8$ -inches stainless steel tubing and led directly to the vent line.

C. Sampling System

The sampling line was $1/4$ -inch stainless steel tubing one foot in length. At the end of the tubing was a $3\frac{1}{2}$ -inch heat exchanger constructed of one inch copper tubing, and water was passed through the shell as coolant. This small heat exchanger was installed to insure complete condensation of the samples. A high pressure needle valve located on the reactor head controlled the rate of flow in the sample line.

D. Chromatograph

A type 26-002 CEC gas chromatograph control unit coupled with a 26-014 CEC analyzer was used to analyze the liquid products. The liquid samples were vaporized in the high temperature analyzer and the separation of the gases occurred in a 10 feet long, $1/4$ -inch diameter stainless steel column packed with butanediol succinate

on Chromosorb. The column packing is often referred to as Craig polyester. The components were differentiated by using thermal conductivity detectors which measured the difference between the thermal conductivity of the carrier gas and the individual components. Helium was used as a carrier gas because of its inertness and high thermal conductivity. The output signal from the detector cell was attenuated and traced on a Leeds & Northrup recorder, where each component was identified by an individual peak. The individual peaks afforded a qualitative analysis, while the peak area afforded a quantitative analysis. The recorder was equipped with a disc integrator, which automatically determined the relative areas of the peaks.

This analytical setup provided a rapid and accurate means of analyzing the chemical constituents encountered in the research, for even minute traces of impurities could be resolved on the chromatograph, and high reproducibility could be obtained with this unit.

E. Distillation Column

A $1\frac{1}{2}$ -inch I.D. column, which was five feet long, and which was packed to a height of 20 inches with 6-mm Berl saddles, was used to purify the heptaldehyde. The distillation pot was of one liter capacity, and this pot was contained in a large heating mantle. The power input to the heating mantle was regulated by a Variac.

F. Refractometer

The purity of the distilled samples was checked using a Bausch-Lomb refractometer which could be read accurately to the fifth decimal place.

III. EXPERIMENTAL

The research was performed in such a manner as to secure the necessary data of a quality that would permit accurate determination of the kinetic quantities in question at various combinations of reaction variables for the hydrogenation of heptaldehyde.

A. Preparation of Reactants

The heptaldehyde used as the reactant was obtained from Distillation Products Industries as a technical grade chemical. The purity of the chemical as received was checked on a refractometer; and certain impurities were suspected to be present, since the index of refraction was extremely high. A value of 1.43147 at 26.2°C was obtained, whereas the literature value for pure material is 1.40972 at this temperature. Also, a slight yellow coloring was present, and pure heptaldehyde is colorless.

The pure heptaldehyde distilled over at 147°C at a pressure of 705 millimeters of mercury along with extremely small traces of water. The water was removed in a separatory funnel, and the index of refraction of the purified heptaldehyde checked to the fourth decimal with the literature value.

The impurities were suspected to be ricinoleic acid and 10-hendecenoic acid, which are the other two components obtained

in the destructive distillation of castor oil (34). The index of refraction of ricinoleic acid and 10-hendecenoic acid are 1.4320 and 1.4501 respectively at 20°C (21). Also, the boiling points of the two acids are 250°C at 15 millimeters of mercury and 275°C at 760 millimeters of mercury in the same respective order. The high boiling fraction began to come over at 272°C and had a deep yellow color, thereby strengthening the conclusion as to the identity of the contaminants.

The copper chromium oxide catalyst was obtained in a reduced form from the Harshaw Chemical Company, catalogue number Cu-1170-T. The catalyst was 1/8-inch by 1/8-inch cylindrical pellets, and the following analysis was supplied by the manufacturer: 33.0% CuO, 38.0% Cr₂O₃, 10.5% BaO, and 18.5% support. The constituents were actually present as CuO, CuCr₂O₄, and BaCrO₄.

B. Laboratory Procedure

The heptaldehyde and catalyst were carefully weighed into the reactor in specified weight ratios. The weighings were made to the nearest 0.1 gram. The reactor was securely bolted into place in the heating jacket, and nitrogen gas was used to purge the system clean of oxygen. A minimum of eight nitrogen purges were used, and with each purge the nitrogen pressure was allowed to build up to 100 psi before the system was bled to 25 psi. Care was always taken to keep the reactor at higher than atmospheric pressure to prevent "back flushing" of the air. When the system

was satisfactorily purged, the nitrogen pressure was set between 35 and 40 psi, and the heating coils were started.

The heating was done rapidly up to within 50°F of the desired reaction temperature, and then a very gradual increase was used to attain the final temperature, care being taken not to "over-shoot" the desired temperature. When the system appeared to be at a thermal equilibrium with the surroundings, that is, when the convection and radiation losses were balanced against heat input, the hydrogen gas was cautiously injected into the system.

The total injection period was between $1\frac{1}{2}$ and 2 minutes, for the reactor was tested for leaks at several pressures on the way to the final maximum pressure. A soap solution was used for the testing purposes. The initial zero time for the reaction was taken to be when the hydrogen was first injected, for the stirrer was operating and the hydrogen was injected directly into the liquid phase.

The temperature of the reactor was maintained within $\pm 5^\circ\text{F}$ of the reaction temperature by adjusting the Variac setting or by passing cooling water through the coils. Only experience allowed one to accurately judge how to change the settings, or what flow rate of water to use.

Samples were withdrawn at equal time increments, usually 15 or 20 minutes apart. The hydrogen inlet valve was closed, and the sample valve was cautiously opened. A brief sudden discharge

took place, and then a small sample bottle was placed under the tubing and a $\frac{1}{2}$ -milliliter sample was withdrawn. This was an adequate size sample for use in the chromatograph. An asbestos glove was used to hold the sample bottle as a precaution against an accidental burn to the operator. The discharge of the hydrogen gas served to "clean out" any portion of a previous sample that may have been left in the sampling tube, thus assuring homogeneity of the samples.

When the reaction was completed the hydrogen bottle valve was closed tightly, and cooling water was run through the reactor at a high flow rate. The warm hydrogen was bled from the reactor, followed by a minimum of ten nitrogen purges. The reactor was then bled to atmospheric pressure, removed from the heating chamber, and broken open for removal of the final reaction mixture.

Immediate cleaning with acetone and detergent and consequent air drying insured the good condition of the reactor. Also, this readied the reactor for the next run.

C. Analysis

The liquid products were analyzed by gas chromatography in which a butanediol-succinate column provided the separation. The detector signals were traced on a Leeds & Northrup recorder. The X axis on the chart represented time, and the Y axis represented the concentration of each component. This allowed a qualitative and quantitative analysis since each component had a definite elution time, and the disc integrator which operates in

conjunction with the recorder permitted integration of the peak areas.

At the beginning of each run standard samples of heptaldehyde and n-heptyl alcohol were injected into the chromatograph to check elution time for the operating conditions being used and to obtain the peak area correction factors.

In order to obtain a mole percent analysis, it was necessary to take the percentage obtained from the peak areas and multiply these values by a correction factor. This correction factor, which varied from day to day, and thereby necessitated the use of standard samples each day, could be obtained from the following formula which was given in the literature (11):

$$\text{Mole fraction of A} = f_a a / (f_a a + f_b b)$$

where

f_a = correction factor for component A

f_b = correction factor for component B

a = integrator counts for component A

b = integrator counts for component B

By assuming either f_a or f_b to be 1.00, thus establishing a "reference base", the other correction factor could be obtained from the standard samples.

The operating conditions of the column were kept as constant as possible for all analyses, namely: temperature at 230°C, carrier gas of helium, column pressure of 40 psi, carrier gas

flow of 60ml/min, and the use of the same column. These conditions affect the retention times of the various components, and all of these conditions except the temperature could be held very constant. The temperature fluctuated between 228°C and 232°C due to the variation in local power output. However, this was a variation in initial condition only and did not occur to any noticeable extent during the actual running of the chromatographs. Only a 1°C temperature variation was noticed during any given analysis period.

A precautionary step of allowing the column to come to thermal equilibrium was always undertaken. This reduced the "drift" of the recorder to a minimum, and the "drift" usually could not be detected except at the most sensitive attenuations.

Each sample was injected into the vaporizer chamber using a 50 microliter syringe. The standard size injection sample was 10 microliters.

The septum on the vaporizer could be punctured between 15 and 20 times before it was necessary to replace it. If it was used more than 20 times "blow-back" occurred. That is, the sample contained in the microsyringe would be blown back at the operator when he was attempting to inject the sample.

Each analysis was allowed to run for twelve minutes, thereby assuring complete resolution of all the components. The heptaldehyde and n-heptyl alcohol would normally be completely eluted in five minutes, but the small trace of water formed in

the surface reduction of the catalyst would not elute before eight minutes.

IV. DISCUSSION OF RESULTS

The results were derived from eight experimental runs in which temperature, pressure, catalyst to reactant ratio, and catalyst size were varied.

A. Thermodynamic Considerations

Calculation of the thermodynamic feasibility of the reaction from free-energy changes at atmospheric pressure was done using the method of Franklin (14), and the results are plotted in Figure 1. The overall free-energy change for the reaction is negative until a temperature of 600°K is reached, and then the aldehyde is seen to possess a lower free-energy value than the alcohol. However, the application of high pressure permits the reaction to proceed even at the higher temperatures. Groggins has emphasized these facts in discussing hydrogenation of the carbonyl group, and supports his statements with additional graphical presentations (19).

B. Reaction Order

It was found that an "induction period" was necessary at 250°F and 300°F before the reaction would proceed smoothly, and this can be observed in Figure 5. At 350°F, this period of induction has apparently vanished, and it can be concluded that the

length of the induction period is a function of the temperature.

Once the induction period had passed, the reaction proceeded according to a zero order rate law with respect to the heptaldehyde until a low concentration of heptaldehyde remained in the reaction mixture. At this point the reaction became first order with respect to the heptaldehyde and remained so until completion of the reaction.

The variation in reaction order was observed during all eight experimental runs regardless of the conditions employed in any given run.

Since the hydrogen was always kept in large excess in the bulk phase, no attempt was made to obtain the order of the reaction with respect to the hydrogen.

C. Controlling Step

Nine steps take place in series, and it is possible for any of them to control the overall rate of reaction. If the rate of any one step is appreciably slower than that of the others, the overall rate will adjust itself to that of the slow step. The slow step is known as the controlling reaction step, and will hereafter be referred to as the rate controlling step. Each step will be considered separately.

1. Gas-Liquid Interface

The transfer of the hydrogen from the gaseous region above the reaction mixture into the bulk liquid phase is influenced

primarily by the solubility of the hydrogen in the liquid. Therefore, the possibility that the transfer of the hydrogen from the gas phase into the bulk liquid phase was controlling was investigated.

Data on the solubility of hydrogen in aldehydes could not be found. Therefore, the solubility in a similar liquid such as an alcohol was used as a criteria in examining this step. Data on the solubility of hydrogen in alcohols up to n-butanol has been published (15), and the graph of this study is presented in Figure 2. The solubility is seen to increase with increasing pressure, and Henry's law is followed with reasonable accuracy for most alcohols. It has also been shown that the solubility of hydrogen in most organic liquids increases with increasing temperature (19).

If the solubility of the hydrogen had been the controlling step, the increase in hydrogen pressure from 800 psi to 1000 psi would have increased the rate. However, the results presented in Figure 7 show that increasing the hydrogen pressure had no effect on the reaction rate. Rather, the curves for 800 psi and 1000 psi fell directly upon one another. It was therefore concluded that this step was not rate controlling.

2. External Diffusion (In)

In a batch reactor the molecular diffusion of the hydrogen to the catalyst surface is very often the dominant factor in the rate controlling mechanism. The rate of mass transfer from the bulk liquid phase to the solid surface can be expressed by the

equation

$$N = k_L a (C_g - C_i)$$

where

N = rate of mass transfer per unit mass of catalyst

k_L = mass transfer coefficient

C_g = concentration of diffusing component in the bulk stream

C_i = concentration of diffusing component at the solid interface

a = external area of catalyst particle per unit mass

The value of $C_g - C_i$ determines the importance of external diffusion in the overall mechanism. By increasing the partial pressure of the hydrogen in the vapor phase the concentration in the bulk liquid phase would increase according to Henry's law, and the rate of the reaction should increase. Increasing the partial pressure of the hydrogen did not increase the reaction rate, and it was concluded that this was not the rate controlling step.

The diffusion of the aldehyde at low conversions was not rate controlling, for the rate would not follow a zero order law if this were the case. By considering the diffusion equation once again, it can be seen that $C_g - C_i$ would have to be constant for a zero order reaction.

When the reaction becomes first order with respect to the aldehyde at high conversions, the diffusional step could become an important factor in the overall rate. This type of behavior is expected with a diffusion controlling step. In addition, the low

activation energy of 1.39 kcal/gmole is highly indicative of a diffusion controlling step.

It is believed that the diffusion of the aldehyde from the bulk liquid phase to the catalyst surface is rate controlling at high conversions. However, additional evidence should be gathered to support this postulation. It is suggested that future efforts be directed at proving or disproving this postulation by varying the superficial velocity of the reactants within the reactor. If diffusion is truly controlling, the change in superficial velocity of the reactants about the catalyst should change the reaction rate (9). However, if no change in reaction rate is observed, the diffusional step could be eliminated as the rate controlling step.

3. Pore Diffusion (In)

The interior surface of the catalyst is more significant than the outside surface, for within the catalyst the vast array of active sites is present.

In order for the inside surface to be effectively used, the reactants must diffuse through the pores to the active sites. The larger the catalyst pellet, the longer is the path of diffusion to the remote interior. A decrease in catalyst size will decrease the path traveled by the diffusing molecules and speed up the reaction if this is the controlling step.

The 1/8-inch catalyst pellets were ground to a 100 mesh size, and the reaction with 1/8-inch pellets was duplicated with

this crushed catalyst. An increase in the rate was observed, but this increase was only of the order of 80 percent. This indicates that pore diffusion might contribute some resistance to the reaction, but that its effect is fairly negligible in contrast to the other steps. The increase in reaction rate is to be expected even if the pore diffusion is not controlling. The increase in surface area brings about an increase in the number of active sites, thus increasing the reaction rate.

It should be noted that the changing of the system pressure could not help answer any questions concerning pore diffusion since it is highly independent of pressure (39).

4. Adsorption of Heptaldehyde

The zero order rate for low conversions would seem to eliminate adsorption of the aldehyde as rate controlling for low conversions. Rate equations based on an adsorption step as rate controlling would contain the concentration of the adsorbed component raised to some power, whether fractional or integral (23, 27).

Consideration of a general adsorption isotherm illustrates that a zero order reaction is typical when the concentration of the adsorbed compound is a constant, as shown in Figure 14. In effect, this is saying that the adsorption step is in equilibrium, and not rate controlling.

At high conversions, the rate becomes first order and adsorption could control. However, the low value of activation energy supports a diffusional step as controlling rather than an

adsorption step.

Oldenburg has shown that in the vapor phase hydrogenation of the C_2-C_4 aldehydes to the corresponding alcohols, the adsorption of the aldehydes was the controlling step (30). However, he employed a nickel catalyst and a differential flow reactor, in which four percent conversion was a maximum. All of his correlations were based on initial rate data, and care must be taken not to rely too heavily on the comparison of vapor phase work to liquid phase work.

5. Adsorption of Hydrogen

In general the adsorption of hydrogen increases substantially with an increase in pressure (42). Therefore, when the hydrogen pressure was increased from 800 psi to 1000 psi the reaction rate would have increased, but this was not observed. Therefore, it was concluded that the adsorption of the hydrogen was not the controlling step.

The vast summary of previous experience with metal and metal oxide catalysts indicates that hydrogen is readily adsorbed on these surfaces, and generally in the atomic state. This adds strength to the argument that the adsorption of the hydrogen is not rate controlling.

6. Surface Reaction

This appears to be the rate controlling step for low conversions. As an example, it can be postulated that the hydrogen

is adsorbed as atomic hydrogen, then the following rate equation can be postulated for the surface reaction:

$$r = k_1 (As)(Hs)^2 - k_{-1} (Bs)(s)^2$$

where

(As) = adsorbed aldehyde concentration

(Hs) = adsorbed hydrogen concentration

(Bs) = adsorbed alcohol concentration

(s) = effective concentration of unreacted active sites

k_1, k_{-1} = rate constants for forward and reverse reactions respectively

However, the contribution of the reverse reaction can be assumed to be negligible, and the second term of the rate equation can be neglected. The rate curves can be explained in the following manner based on this form of the surface reaction. As the reaction proceeds at low conversions, the rate remains constant, for the relative amounts of As and Hs remain fixed. That is to say, the adsorption steps are in equilibrium and the rate is merely a function of how rapidly the surface reaction takes place.

Furthermore, this type of rate behavior would be exhibited for the surface reaction controlling even if the hydrogen were not dissociated, but reacted as adsorbed molecular hydrogen, or reacted in the bulk phase.

At high conversions, the rate becomes first order with respect to the aldehyde concentration, and the activation energy

decreases to a value of 1.39 kcal/gmole. This change in reaction order, and especially the substantial decrease in the value of the activation energy, suggests a change in the controlling step. The low value of the activation energy suggests ruling out the continuance of the surface reaction as the controlling step.

7. Desorption of n-Heptanol

The rate equation based on the desorption of the alcohol as a controlling step would not be zero order, since the concentration of the alcohol would appear in the equation.

In addition, by applying the Lewis theory of acids and bases to the electronic structure of the alcohol and aldehyde, it can be seen that the aldehyde is more basic, that is, a better electron donor. The metallic catalyst surface has a greater affinity for the aldehyde, since it is an electron acceptor. This helps promote the rapid desorption of the alcohol.

8. Pore Diffusion (Out)

The same statements made under pore diffusion (in) will apply in this case and therefore no further comment is necessary.

9. External Diffusion (Out)

When the rate equation was zero order, diffusion could not be the controlling step, since the rate equation would contain the concentration of the alcohol to some power.

When the reaction becomes first order at high conversions, the diffusion of the alcohol from the interface to the bulk liquid

phase could become an important factor in the overall rate.

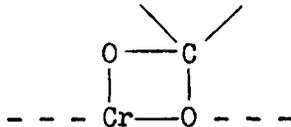
It can not be proven from the data obtained whether this diffusional resistance is due to the inward diffusion of the reactant, or outward diffusion of the product. It can only be postulated that the diffusion of the alcohol could be a significant contributing factor to the overall resistance.

10. Summary of Steps

A tabular summary of the nine steps considered would be helpful at this point in presenting a clearer picture of the overall situation. This tabular summary can be found in the Appendix, Table X.

D. The Catalyst

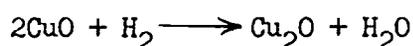
The mechanism by which the copper chromite catalyst operates has been postulated by Cram (10). It is a highly selective catalyst, and the selectivity arises from the adsorption of the polar carbonyl function on the metal oxide surface as illustrated below



Barium oxide is added to the catalyst to serve as a promoter. The purpose of the promoter is to substitute into the lattice of the catalyst crystal and cause distortion (45). Since the active sites on the surface are believed to be a function of lattice defects, the promoters effectively increase the number of

active sites.

The copper oxide was present originally as the black cupric oxide. Evidence of surface reduction to cuprous oxide is twofold, since the reddish color of the lower valence oxide is present at the end of the reaction, and the appearance of small traces of water in the chromatograms suggests the following reaction:



The sample chromatogram shown as Figure 4 indicates the water peak.

The apparent induction periods, which appeared at 250°F and 300°F, support the theory that surface reduction of the catalyst is necessary before the reaction can proceed. The length of these induction periods should be a function of the system temperature, since reduction is a function of temperature, and the data presented in Figure 5 illustrates the length of the induction period.

E. Side Reactions

Although several earlier investigators obtained products other than n-heptanol from this type of reaction, regardless of the catalyst employed, only once did a side product appear in this work. (31, 43).

This product was not identified and was present as 5 parts in 8000, which is extremely small. The chromatograph peak for this product appeared between the heptaldehyde and n-heptanol peaks. As reported in an earlier work (43), n-hexane was found

to be a reaction product. However, in using the normal column operating conditions, the n-hexane would have been resolved one minute before the heptaldehyde and not between the two reaction components.

V. SUMMARY

In the past the catalytic hydrogenation of aldehydes to the corresponding alcohols was a subject of interest primarily in organic chemistry, which was generally concerned with percentage yields rather than the kinetics of the reaction. As new industrial processes take shape, the chemical engineer must search further than yield percentages, for he is concerned with equipment design and the economics of any given process. Kinetic data becomes an indispensable tool in evaluating any chemical process.

The lack of kinetic data on the hydrogenation of aldehydes above butyraldehyde prompted this study. Since heptaldehyde is a natural product obtained from castor oil, it seemed logical that it should be the aldehyde chosen for study.

In a gas-liquid reaction catalyzed by a solid, several variables influence the reaction kinetics: temperature, pressure, the catalyst employed, and agitation rate. By changing these variables in varying degrees, the rate controlling step of the reaction can be found and the scaling-up of reaction equipment from bench scale to pilot plant can be made from the rate equations thus obtained.

A small high pressure reactor which was especially constructed for hydrogenation work was employed in this research.

The equipment allowed each variable to be changed from run to run, thus affording a good series of kinetic tests.

The reactions were run at temperatures of 250°F, 300°F, and 350°F. Pressure was varied from 800 psi to 1000 psi, and catalyst to reactant ratio on a mass basis was varied from 1:10 to 2.5:10. The 1/8-inch catalyst pellets were employed in all but one run in which the catalyst was crushed to 100 mesh.

Liquid products were analyzed by chromatography which gave an accurate analysis of the heptaldehyde and n-heptyl alcohol along with trace amounts of water formed in the surface reduction of the copper chromite catalyst.

The reaction was found to follow a zero order rate law until low aldehyde concentrations where a first order rate law took over. At a pressure of 1000 psi, the specific reaction rate constants for the zero order rate and for a catalyst to reactant weight ratio of 1:10 (1/8-inch pellets employed) were as follows:

$$k_{350} = 21.5 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

$$k_{300} = 9.95 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

$$k_{250} = 6.31 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

The apparent activation energy from the Arrhenius plot, see Figure 9, was 7.56 kcal/gmole. By changing the pressure to 800 psi, but keeping all other variables constant, the k at 350°F was found to be the same as for the 1000 psi case.

For the first order rate law, the following specific react-

ion rate constants were calculated using the 1:10 weight ratio and a pressure of 1000 psi:

$$k_{350} = 2.07 \times 10^{-3}/\text{min-gm catalyst}$$

$$k_{300} = 1.47 \times 10^{-3}/\text{min-gm catalyst}$$

The apparent activation energy was 1.39 kcal/gmole, as shown in Figure 10.

Crushing the catalyst to 100 mesh resulted in increasing the rate by about 80 percent. At 1000 psi, 350°F, and a 1:10 catalyst to reactant weight ratio, the specific reaction rate constant for the zero order part was 4.39×10^{-4} lbmole/ft³-min-gm catalyst. For the first order rate part, the specific reaction rate constant was 4.13×10^{-3} /min-gm catalyst. At 1000 psi, 350°F, and a 2.5:10 catalyst to reactant weight ratio for the pellets, the specific reaction rate constant for the zero order part was 2.07×10^{-4} lbmole/ft³-min-gm catalyst.

Increasing the temperature increased the reaction rate, yet an increase in pressure had no apparent effect upon the rate. The crushed catalyst and higher catalyst to reactant ratio resulted in an increased reaction rate as expected.

Nine physical steps were considered as rate controlling possibilities, and the experimental data suggested that the surface reaction controlled at low conversions. However, at high conversions the adsorption step could have controlled, the diffusion of the aldehyde from the bulk liquid to the catalyst surface

could have controlled, or the diffusion of the alcohol from the catalyst surface into the bulk liquid could have controlled. The data does not clearly indicate which of these steps did control.

The chromatograph was capable of detecting 1 part in 10,000 of either component and gave very satisfactory results. From the analyses it can be seen that 99.9 percent conversion of the n-heptanal to n-heptyl alcohol can be obtained with the copper-chromium oxide catalyst.

VI. ACKNOWLEDGMENTS

The author gratefully acknowledges the encouragement given by the faculty of the Department of Chemical Engineering of the University of Arizona during the course of this work. Through the grant of a graduate assistantship, the Department's financial support of the research project, and the continuance of an academic scholarship from the Los Angeles Times, the year of graduate study was made possible. Special appreciation is extended to Dr. Robert A. Damon for his guidance as director of this research, and for the many additional hours of help he extended beyond that normally rendered by a thesis director. The critical comments and helpful suggestions of Professors Edward Freeh, Neil Cox, and Ray Richardson were greatly appreciated.

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APPENDIX

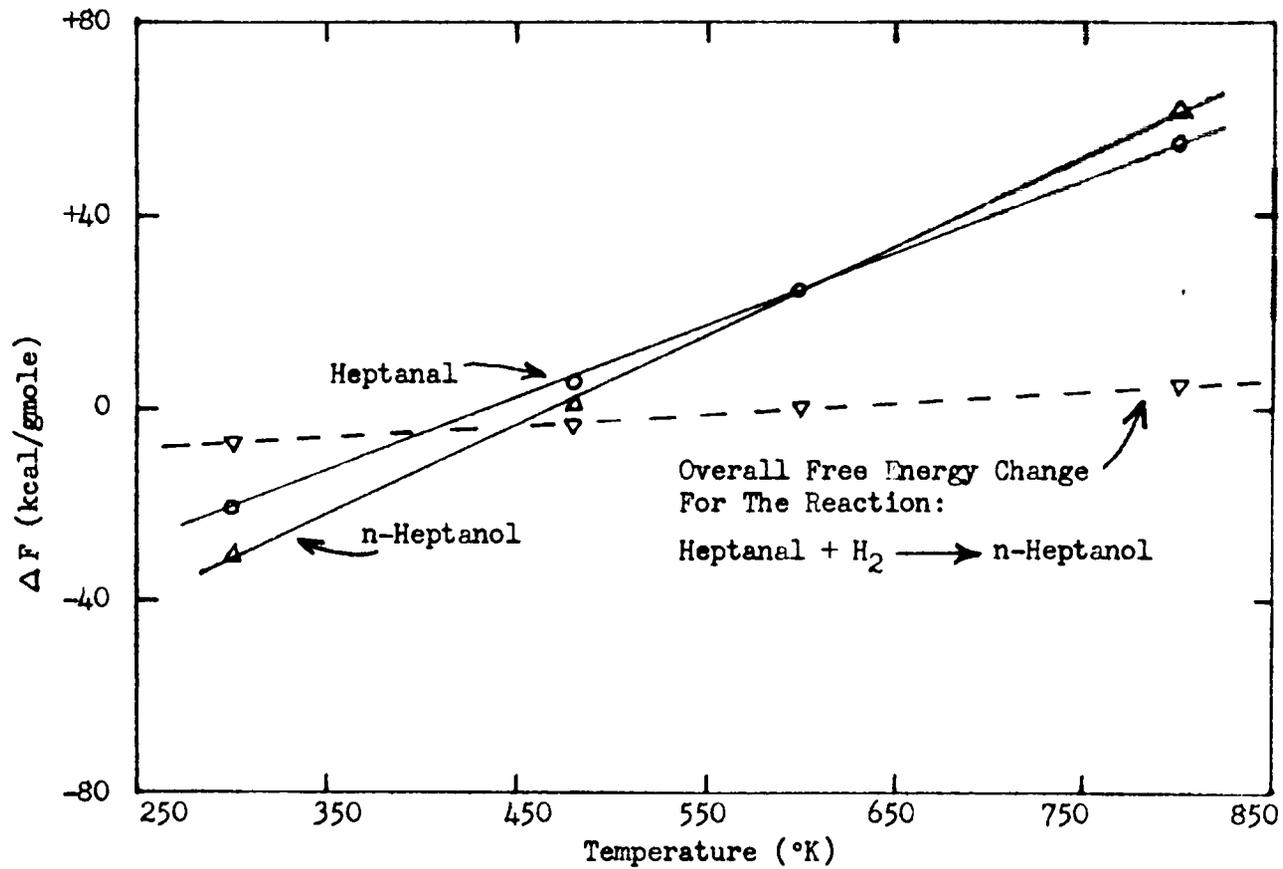


Figure 1: Free Energies of Heptanal and n-Heptanol

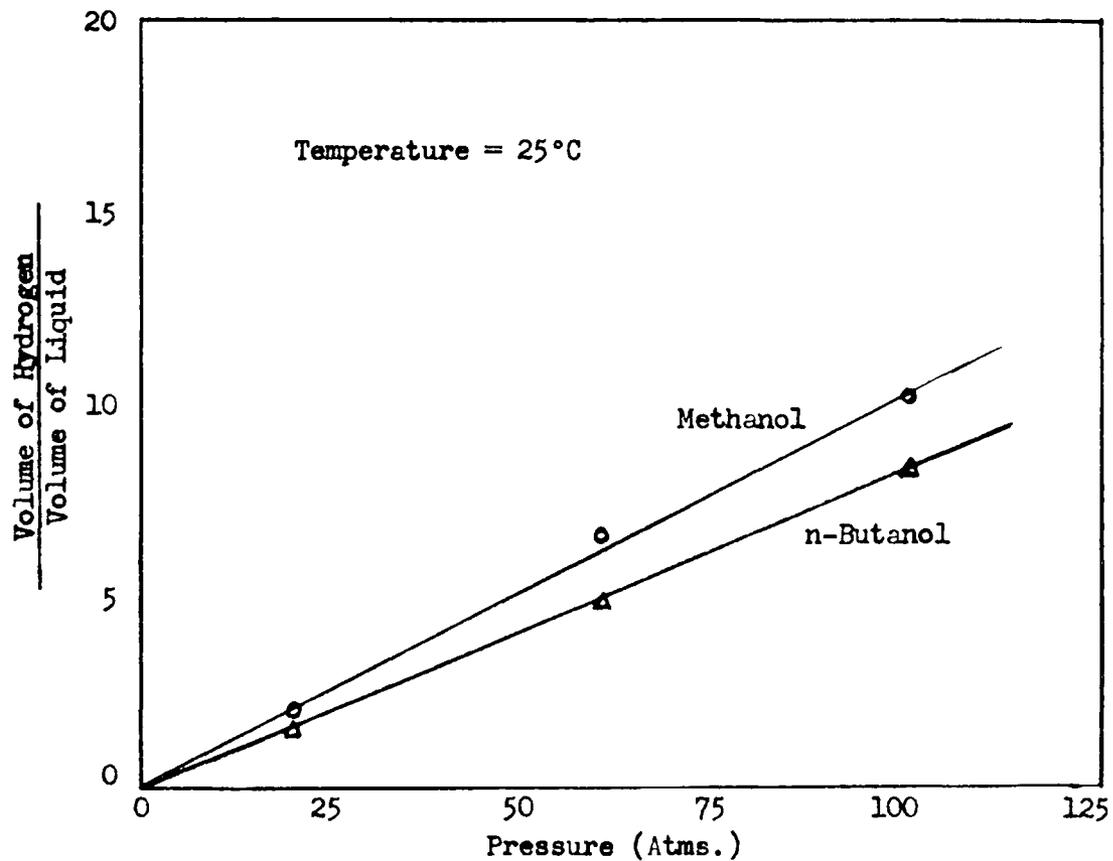


Figure 2: Hydrogen Solubility in Alcohols

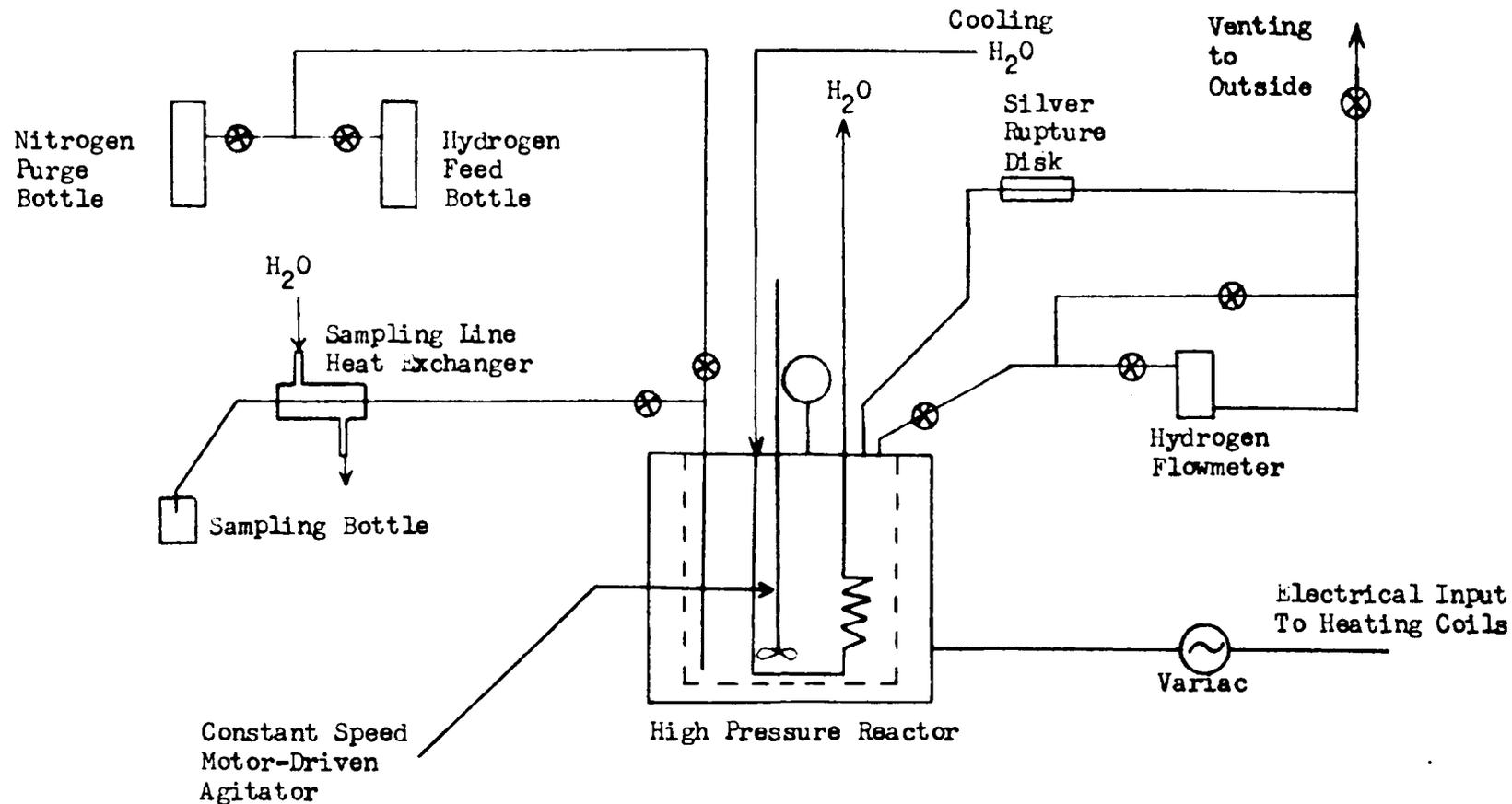


Figure 3: Schematic Flow Diagram of Experimental Process

COLUMN: BUTANEDIOL SUCCINATE
CARRIER: HELIUM @ 60ML./MIN.
COLUMN PRESSURE: 40 PSI
COLUMN TEMPERATURE: 230°C

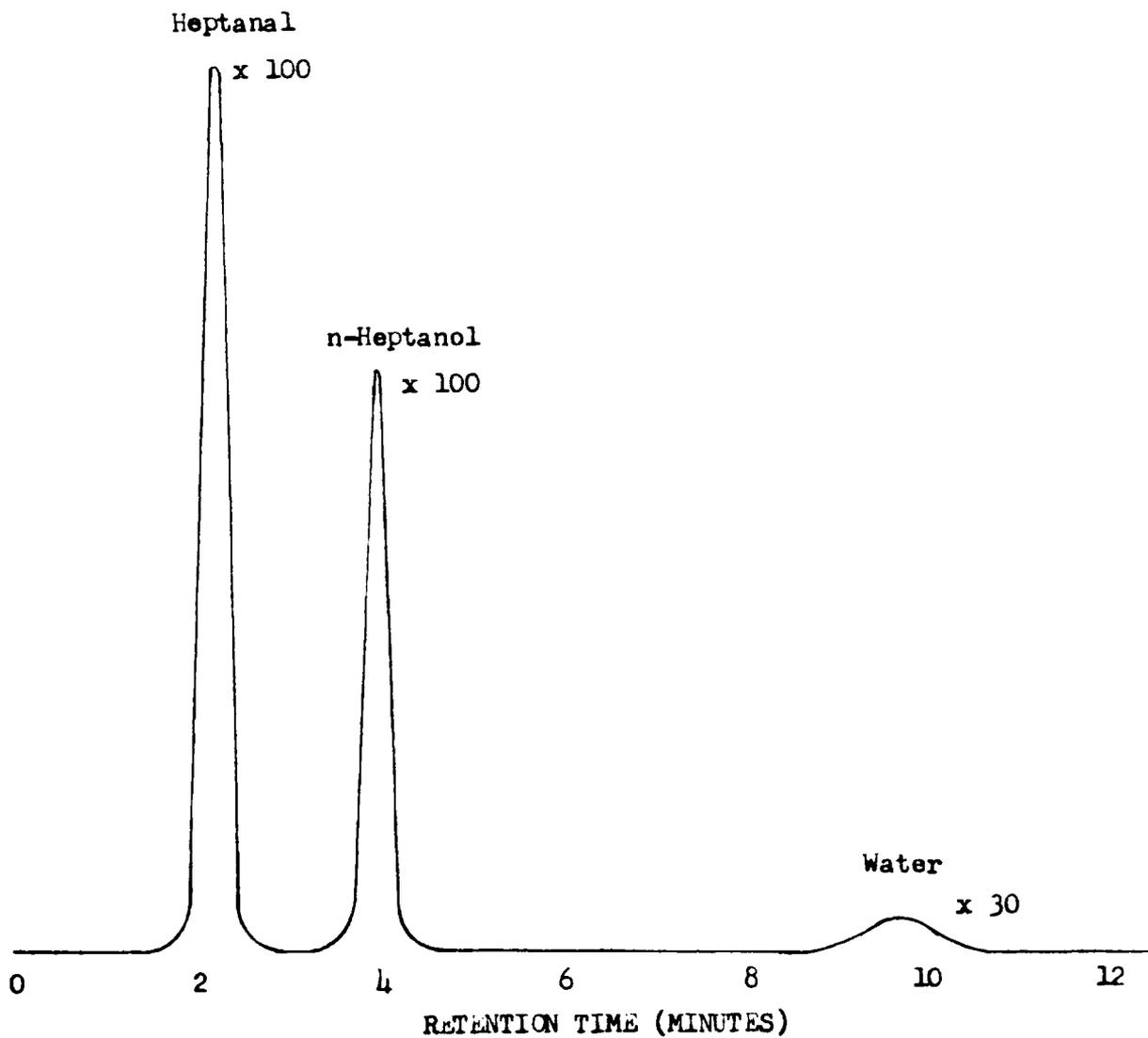


Figure 4: Sample Chromatogram of Reaction Mixture

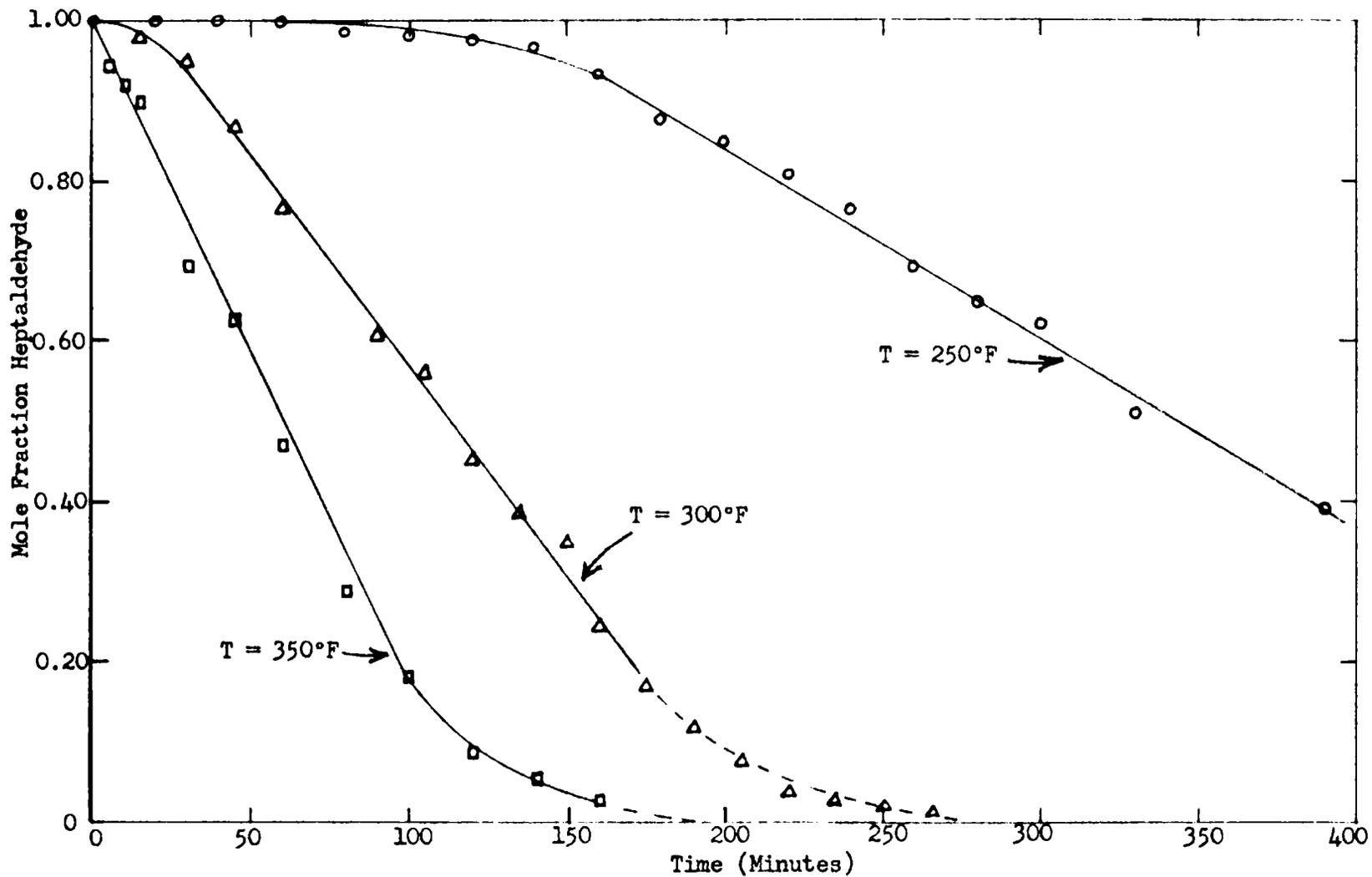


Figure 5: Heptanal Concentration vs. Time at 1000 psi

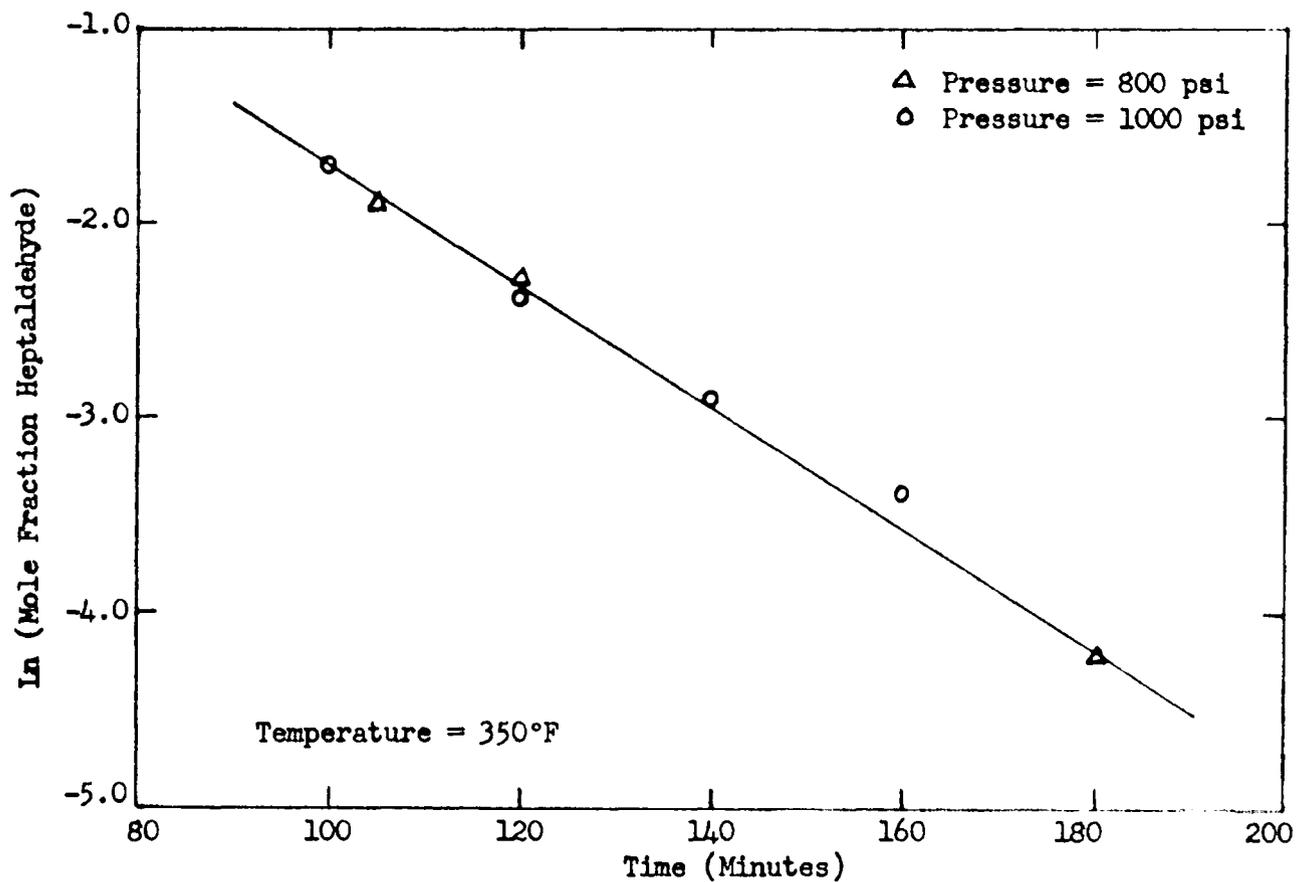


Figure 6: First Order Plot for 1000 psi and 800 psi

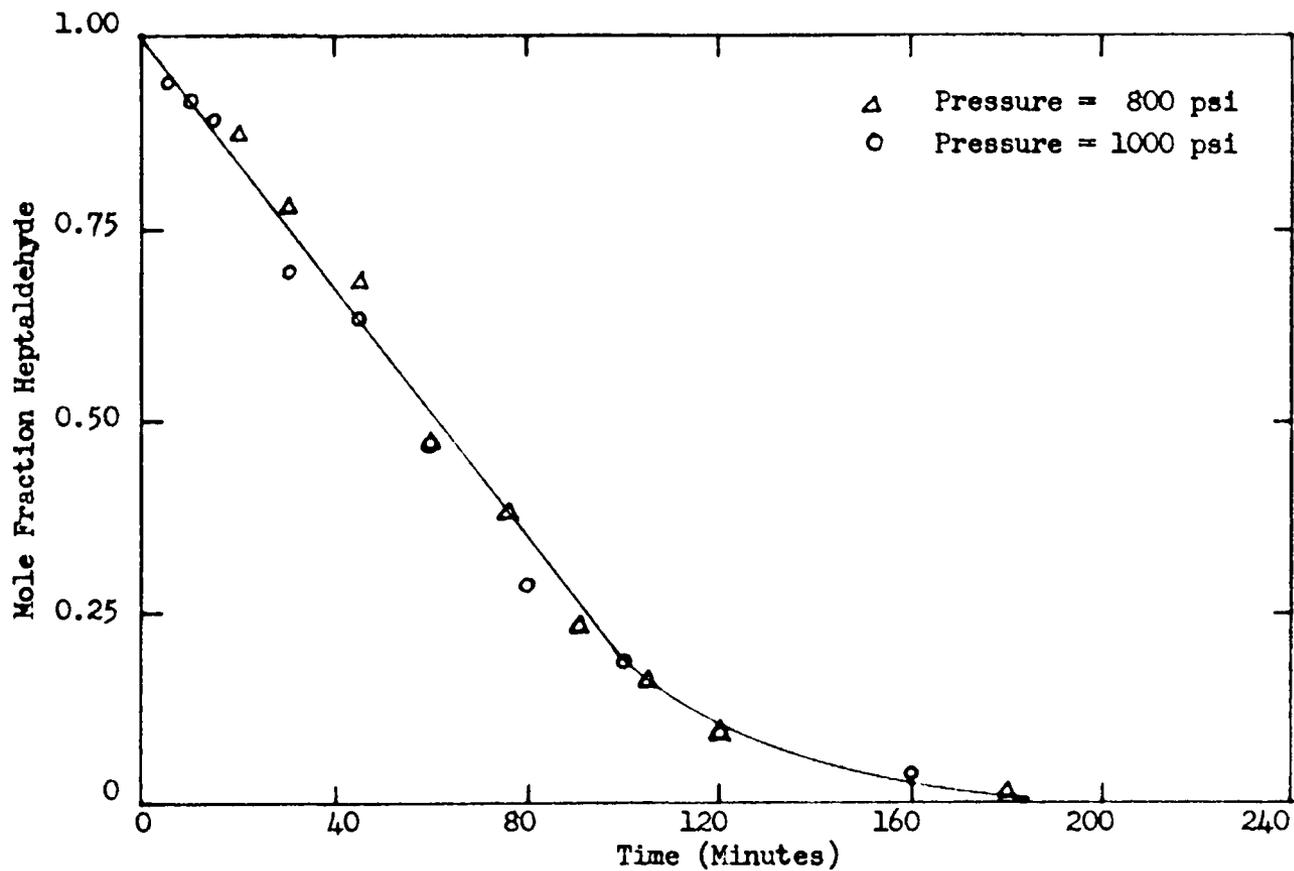


Figure 7: Heptanal Concentration vs. Time at 800 psi & 1000 psi

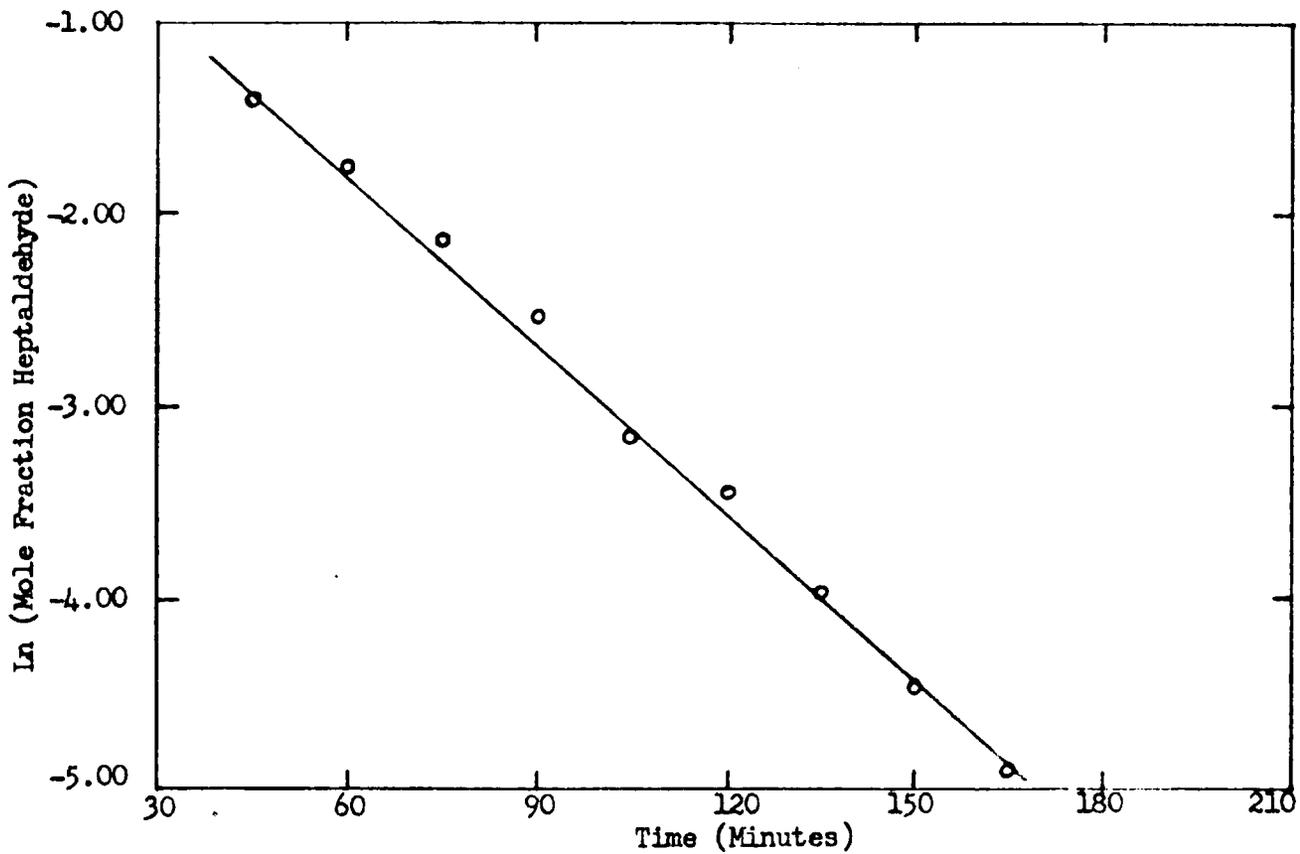


Figure 8: First Order Plot for 1000 psi at 300°F

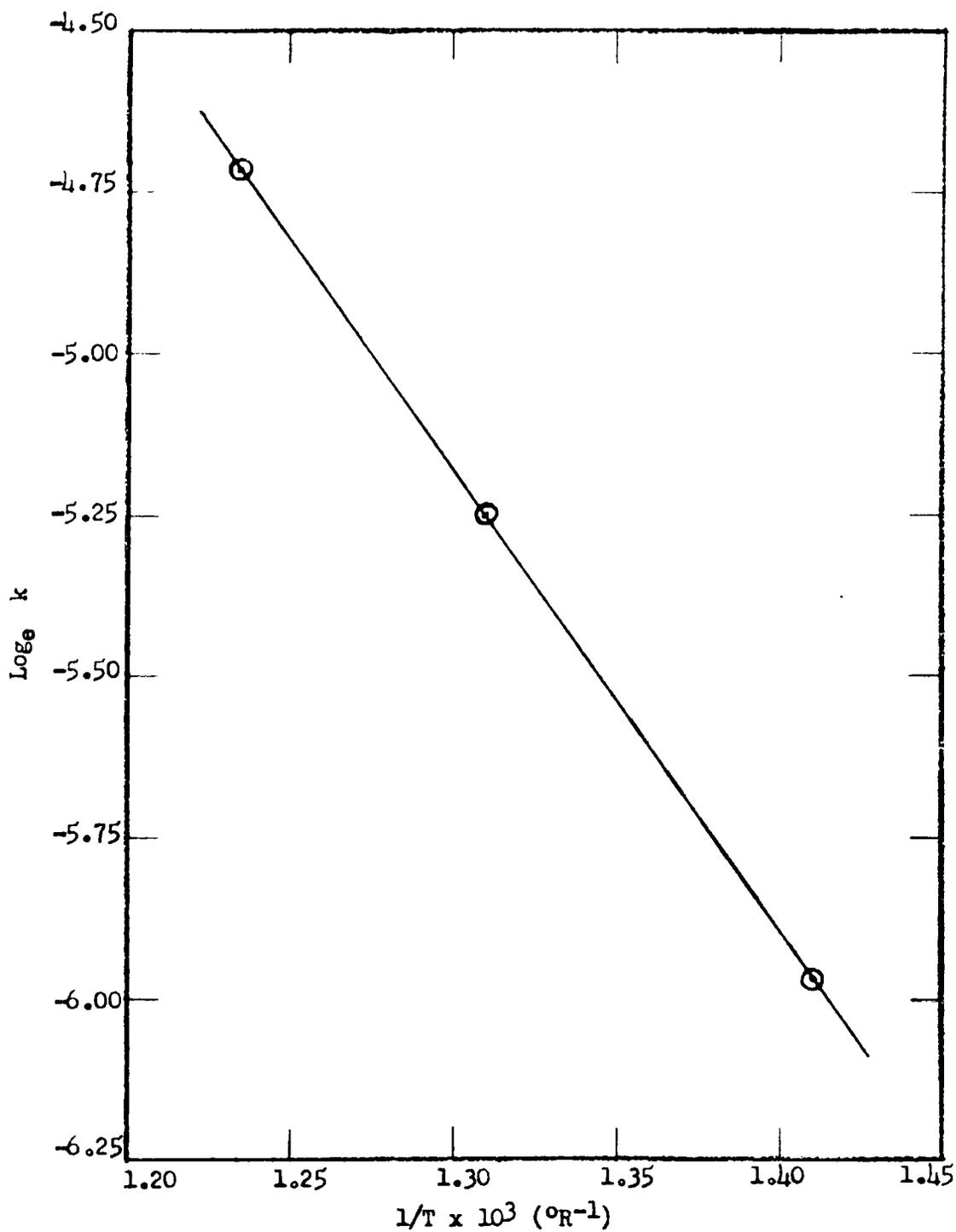


Figure 9: Arrhenius Plot for Zero Order Reaction @ 1000 psi

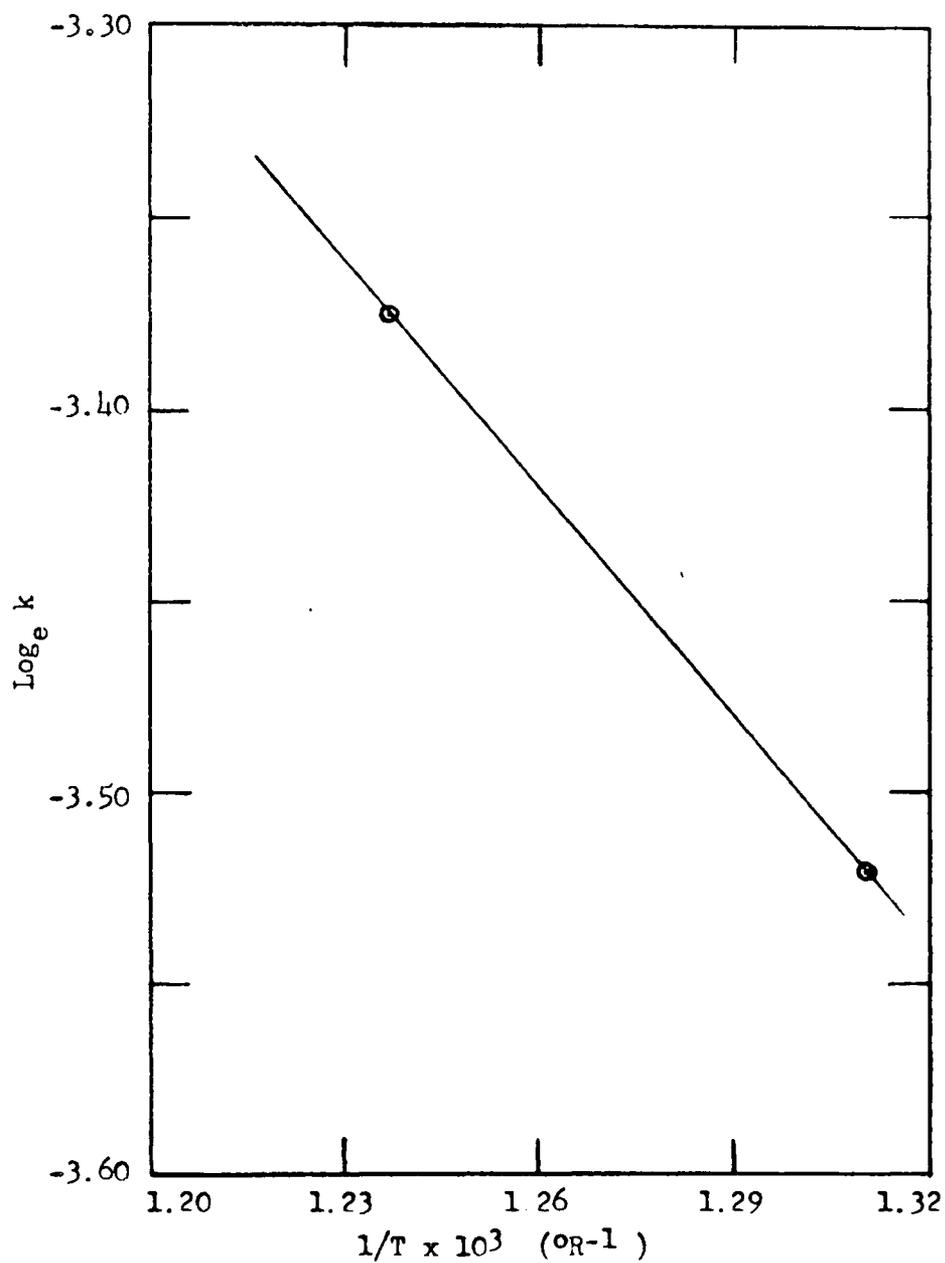


Figure 10: Arrhenius Plot for First Order Reaction @ 1000 psi

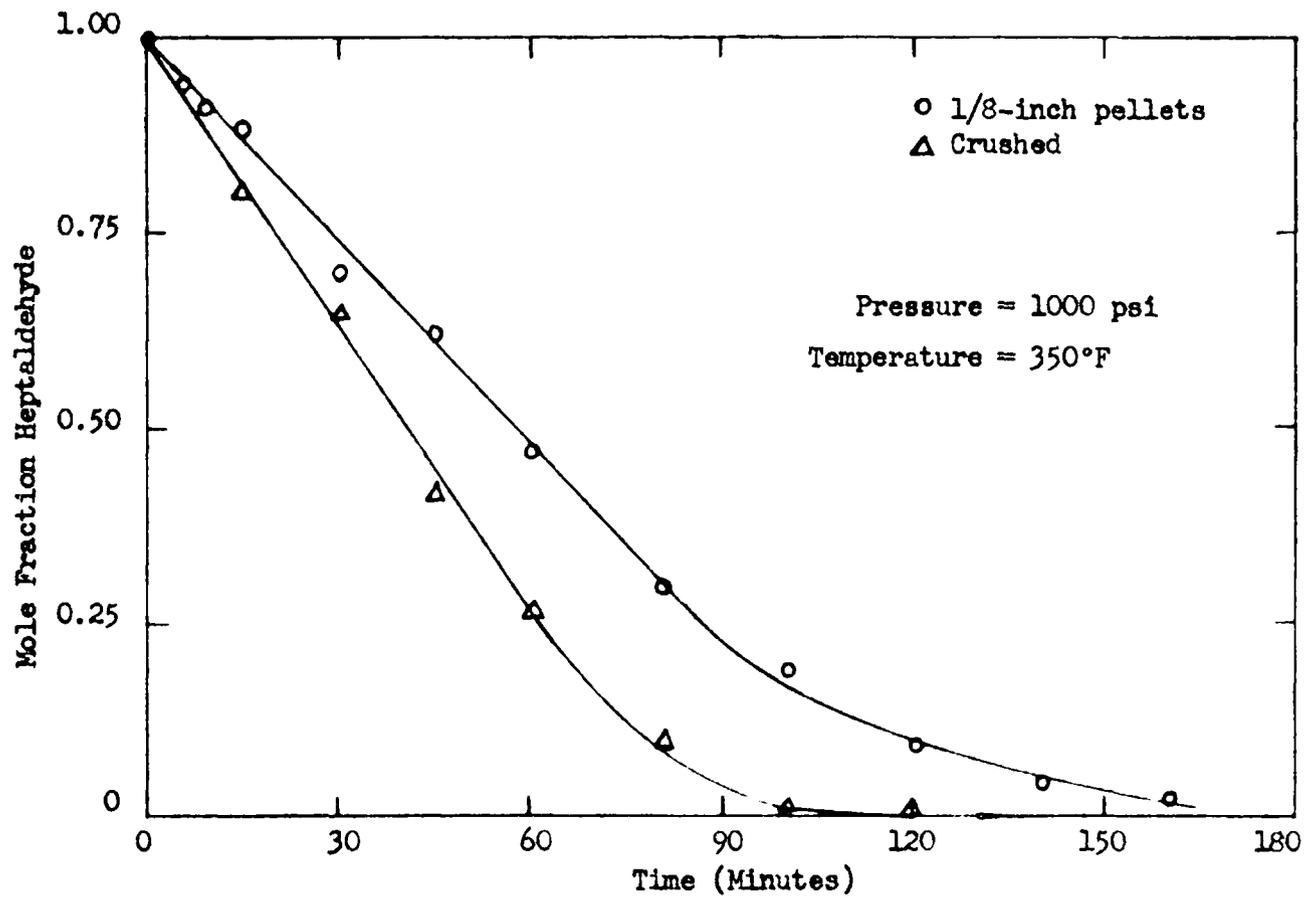


Figure 11: Reaction Rates for Crushed & Pellet Catalyst

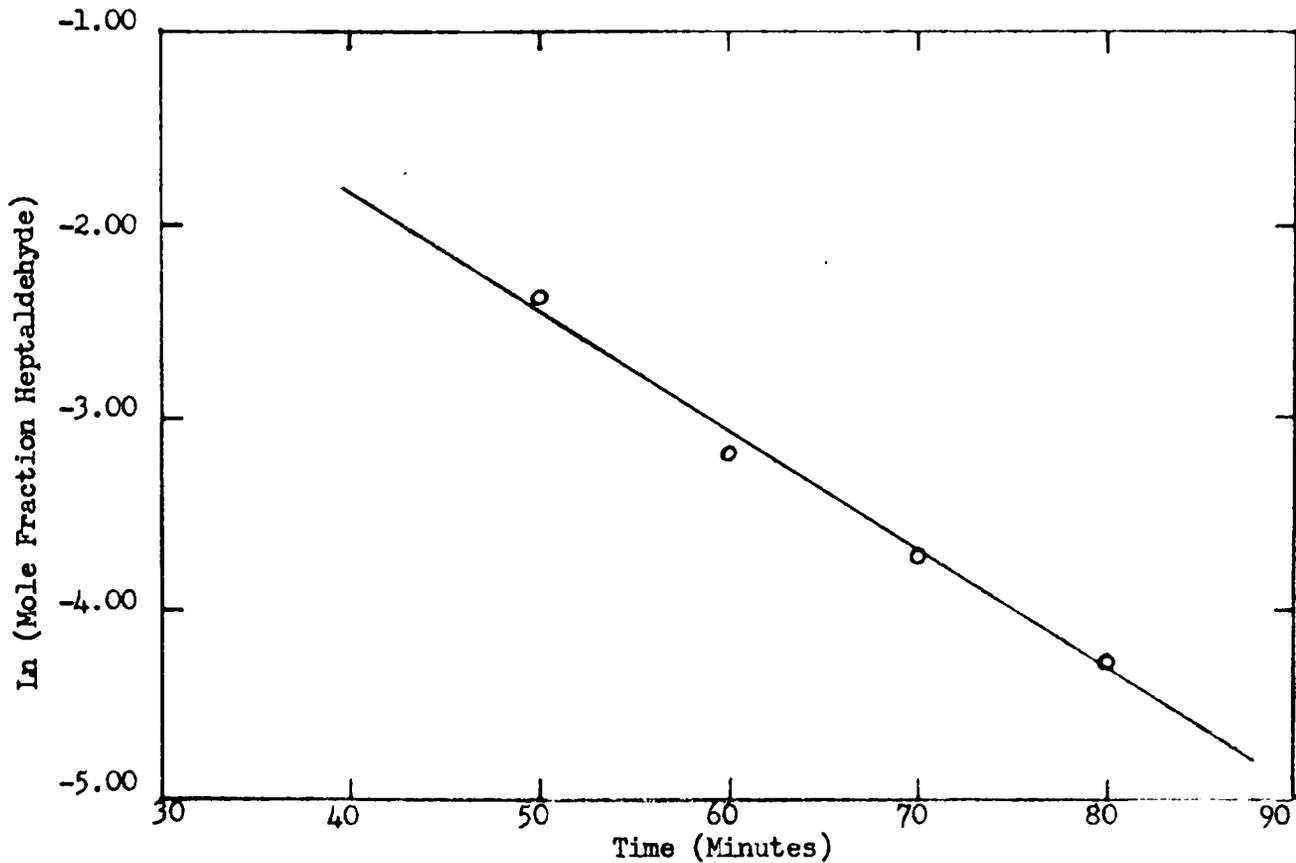


Figure 12: First Order Plot for 1000 psi at 350°F
(High Catalyst Ratio)

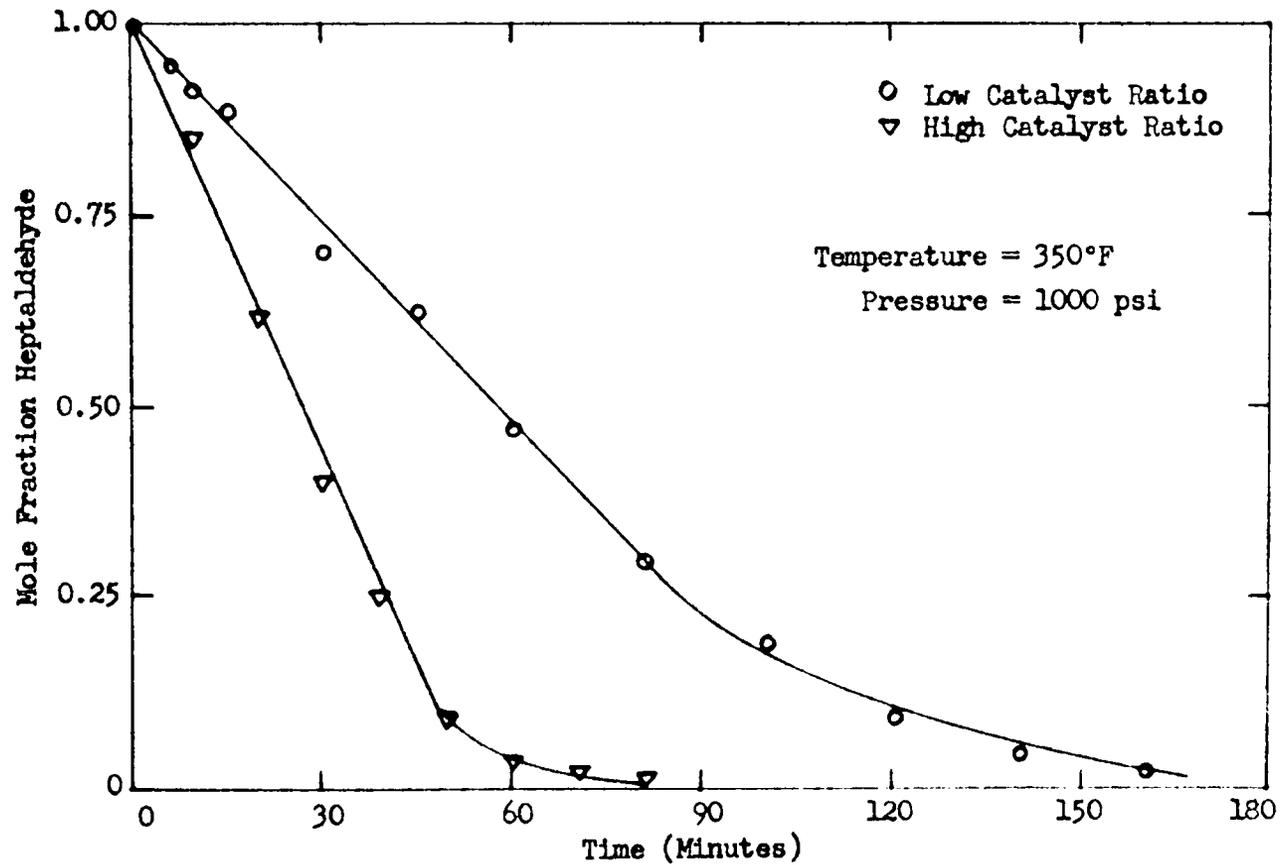


Figure 13: Reaction Rates for High and Low Catalyst Ratios

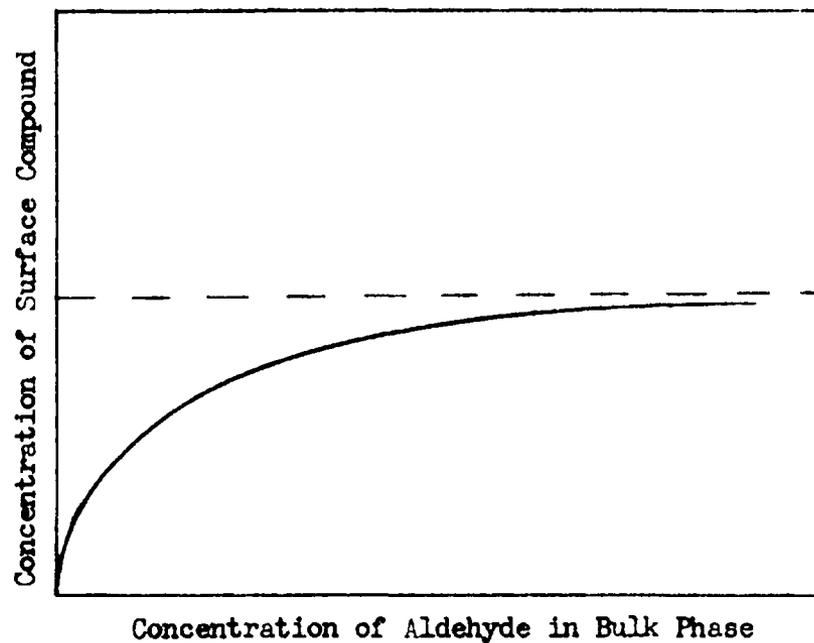


Figure 14: Generalized Adsorption Isotherm Equilibrium Curve

TABLE I
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	250	1000	1.000
20	250	1000	1.000
40	250	1000	1.000
60	250	1000	1.000
80	250	995	0.988
100	250	1000	0.986
120	250	1000	0.976
140	250	1000	0.966
160	255	1000	0.922
180	250	1000	0.877
200	250	1000	0.853
220	250	1000	0.807
240	255	1005	0.768
260	250	1000	0.687
280	250	1000	0.660
300	250	1000	0.628
330	255	1005	0.503
390	250	1000	0.391

Initial Quantities Used:

a.) 170.4 grams heptanal

b.) 17.0 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

TABLE II
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	300	1000	1.000
15	300	1020	0.984
30	300	1000	0.952
45	300	1005	0.865
60	295	1000	0.764
90	300	1000	0.601
105	295	1000	0.566
120	300	1010	0.456
135	300	1005	0.385
150	300	1000	0.350
165	305	1005	0.240

Initial Quantities Used:

- a.) 203.3 grams heptanal
- b.) 20.3 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

TABLE III
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	350	1000	1.000
5	345	1000	0.938
10	350	1000	0.918
15	350	1000	0.895
30	350	1000	0.693
45	350	1000	0.633
60	350	1000	0.468
80	345	1000	0.285
100	345	995	0.182
120	350	1000	0.092
140	350	1000	0.056
160	345	1000	0.033
180	350	1000	0.032 **

Initial Quantities Used:

- a.) 156.7 grams heptanal
- b.) 15.7 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

** This point was discarded from the data due to the fact that the chromatogram of this sample did not yield the sharpness normally exhibited by the samples. It was concluded that this point was unreliable.

TABLE IV
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	350	1000	1.000
10	350	1000	0.913
15	355	1000	0.847
30	350	995	0.656
45	355	1000	0.406
60	350	1000	0.201
80	355	1000	0.089
100	345	1000	0.010
120	350	1000	0.004

Initial Quantities Used:

- a.) 151.0 grams heptanal
- b.) 15.1 grams 100-mesh catalyst

* Nitrogen Partial Pressure = 60 psi

TABLE V
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	350	800	1.000
10	350	800	0.944
20	355	800	0.879
30	350	800	0.794
45	350	800	0.676
60	365	800	0.466
75	350	800	0.388
90	350	800	0.231
105	350	800	0.160
120	350	800	0.098
180	350	800	0.014

Initial Quantities Used:

- a.) 169.2 grams heptanal
- b.) 16.9 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

TABLE VI
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	350	1000	1.000
10	350	995	0.849
20	355	1000	0.616
30	350	1000	0.403
40	350	1000	0.264
50	350	1000	0.091
60	350	1000	0.042
70	350	1000	0.026
80	350	1000	0.014

Initial Quantities Used:

a.) 170.4 grams heptanal

b.) 42.5 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

TABLE VII
REACTION VARIABLES AND CONVERSION TO HEPTANOL

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	300	1000	0.403
15	300	1000	0.358
30	300	1000	0.332
45	300	1000	0.243
60	300	1000	0.172
75	300	1000	0.116
90	305	1005	0.076
105	300	1000	0.039
120	300	1000	0.028
135	300	1000	0.019
150	300	1000	0.011
165	300	1000	0.007

Initial Quantities Used:

- a.) 60.0 grams heptanal
- b.) 90.0 grams n-heptyl alcohol
- c.) 15.0 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

TABLE VIII
REACTION VARIABLES AND CONVERSION TO HEPTANOL **

Time (Min)	Temperature (°F)	Pressure* (psi)	Mole Fraction Heptanal
0	350	1000	1.000
20	350	1005	0.671
40	350	1000	0.533
60	345	1000	0.477
80	350	1000	0.264

Initial Quantities Used:

- a.) 155.0 grams heptanal
- b.) 15.5 grams 1/8-inch catalyst pellets

* Nitrogen Partial Pressure = 60 psi

** The results of this run were discarded due to the fact that the reactor had overheated to 425°F prior to being cooled down to reaction temperature. At 83 minutes reaction time, the silver rupture disc broke, and the reaction was halted. At the time of the rupture, the pressure gauge on the reactor read 1000 psi. Hence, it was concluded that the disc contained an imperfection.

TABLE IX
SPECIFIC REACTION RATE CONSTANTS & ACTIVATION ENERGIES

A. System Pressure: 1000 psi

Catalyst/Reactant Weight Ratio: 1:10

Catalyst: 1/8-inch pellets

Zero Order Reaction:

$$k_{350} = 21.5 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

$$k_{300} = 9.95 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

$$k_{250} = 6.31 \times 10^{-5} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

$$E_a = 7.56 \text{ kcal/gmole}$$

First Order Reaction:

$$k_{350} = 2.07 \times 10^{-3}/\text{min-gm catalyst}$$

$$k_{300} = 1.47 \times 10^{-3}/\text{min-gm catalyst}$$

$$E_a = 1.39 \text{ kcal/gmole}$$

B. System Pressure: 1000 psi

Catalyst/Reactant Weight Ratio: 1:10

Catalyst: 100 mesh powder

Zero Order Reaction:

$$k_{350} = 4.39 \times 10^{-4} \text{ lbmole/ft}^3\text{-min-gm catalyst}$$

First Order Reaction:

$$k_{350} = 4.13 \times 10^{-3}/\text{min-gm catalyst}$$

TABLE X
SUMMARY OF RATE CONTROLLING STEPS

Rate Controlling Step Considered	Controlling For Low Conversions	Controlling At High Conversions	Controlling At All Times
Transfer of hydrogen from gas phase to bulk liquid phase	No	No	No
External diffusion of the hydrogen	No	No	No
External diffusion of the aldehyde	No	Possible	No
Pore diffusion (In)	No	No	No
Adsorption of the hydrogen	No	No	No
Adsorption of the aldehyde	No	Possible	No
Surface reaction	Yes	No	No
Desorption of the alcohol	No	No	No
Pore diffusion (Out)	No	No	No
External diffusion of the alcohol	No	Possible	No

TABLE XI
PHYSICAL PROPERTIES OF N-HEPTANOL

1. BOILING POINT:

Temperature (°C)	Pressure (mm Hg)	Reference No.
176.4	760.0	12
176.0	760.0	21
176.0	758.0	13
175.9	759.5	37
175.4	760.0	26
174.4	751.2	44
84.7	20.0	37

2. MELTING POINT:

Temperature (°C)	Reference No.
-34.03	26
-34.1	12
-34.6	21

3. CRITICAL TEMPERATURE:

Temperature (°C)	Reference No.
248.5	13

4. DENSITY: (All reference to water at 4°C)

Density (Gm./ML.)	Temperature (°C)	Reference No.
0.83622	0	12
0.83590	0	37
0.82601	15	12
0.8260-	15	37
0.8231-	20	35
0.8227-	20	37
0.8223-	20	13
0.8219-	20	21
0.81583	30	12
0.8116-	34.6	44

5. INDEX OF REFRACTION:

Index of Refraction	Light Source	Temperature (°C)	Reference No.
1.4249-	D line	20	13
1.4245-	D line	20	37
1.4241-	D line	20	21
1.42190	He red	20	37
1.42456	He yellow	20	37
1.43043	He green	15	37
1.43002	He green	15	12
1.42351	He red	15	37
1.42310	He red	15	12
1.42627	He yellow	15	37
1.42567	He yellow	15	12
1.42874	He green	20	37
1.43424	He violet	15	12
1.42347	H alpha	15	12
1.43102	H beta	15	12
1.43520	H epsilon	15	12

6. THERMAL CONDUCTIVITY:

Thermal Conductivity	Units	Temperature (°C)	Reference No.
0.000383	CGS	30	38
0.000377	CGS	60	38
0.000369	CGS	100	38
0.0903	BTU	100 (°F)	7

7. SURFACE TENSION:

Surface Tension (Dynes/Cm.)	Temperature (°C)	Reference No.
24.84	15	20
24.42	20	20
23.61	30	20

8. VAPOR PRESSURE: (Reference No. 21)

P (mm. Hg)	1	10	40	100	400	760
Temp. (°C)	42.4	74.7	99.8	119.5	155.6	175.8

9. THERMODYNAMIC PROPERTIES: (Reference No.18)

Temp. (°C)	(H°-H₃)T cal./deg.	S° cal./deg.	C _p ^o cal./deg.	- H _f ^o kcal	Log K _f ^o
273	26.55	111.26	40.11	80.89	28.35
298	27.80	114.83	42.70	81.65	22.93
300	27.88	115.07	42.91	81.71	22.56
400	32.98	128.79	53.62	84.52	7.42
500	38.12	141.82	63.51	86.83	- 1.94
600	43.05	154.08	71.92	88.68	- 8.34
700	47.67	165.69	79.15	90.11	-12.99
800	52.02	176.69	85.32	91.13	-16.54
900	56.04	187.02	90.65	81.80	-19.31
1000	59.72	196.83	95.25	92.23	-21.54

10. N-HEPTANOL - N-HEPTANAL SYSTEM: (Reference No. 26)

Mole Fraction Heptanol	Freezing Point (°C)
0.000	-43.71
0.037	-46.11
0.074	-50.44
0.143	-48.15
0.187	-34.52
0.238	-19.69
0.296	- 7.85
0.353	- 1.98
0.401	0.33
0.456	1.57
0.489	2.25
0.594	0.47
0.662	- 4.16
0.715	-10.31
0.777	-26.04
0.794	-32.97
0.829	-44.92
0.849	-49.06
0.877	-45.27
1.000	-34.03

11. SOLUBILITY IN WATER: (Reference No. 16)

Temp. (°C)	18	70	80	90	100	110	120
<u>Gm. Heptanol</u> 100 Gm. Soln.	.100	.125	.170	.225	.285	.355	.430

TABLE XII
PHYSICAL PROPERTIES OF HEPTANAL

1. BOILING POINT:

Temperature (°C)	Pressure (mm Hg)	Reference No.
155.0	760.0	21
152.8	760.0	12
152.8	760.0	26
59.6	30.0	37

2. MELTING POINT:

Temperature (°C)	Reference No.
-45.0	21
-43.71	26
-43.3	12

3. DENSITY: (All referenced to water at 4°C)

Density (Gm./ML.)	Temperature (°C)	Reference No.
0.83423	0	12
0.8252-	15	37
0.82162	15	12
0.850--	20	21
0.82190	20	37
0.80902	30	12

4. SURFACE TENSION:

Surface Tension (Dynes/Cm)	Temperature (°C)	Reference No.
27.04	15	20
26.58	20	20
25.68	30	20

5. VISCOSITY:

Viscosity (Poise)	Temperature (°C)	Reference No.
0.00977	15	41
0.00791	30	41

6. INDEX OF REFRACTION:

Index of Refraction	Light Source	Temperature (°C)	Reference No.
1.4131-	D line	20	21
1.41247	He red	15	12
1.41952	He green	15	12
1.41511	He yellow	15	12
1.42378	He violet	15	12
1.41282	H alpha	15	12
1.42044	H beta	15	12
1.42471	H epsilon	15	12

$dn/dt = 0.00054/^\circ\text{C}$ for D line

7. SPECIFIC HEAT:

C_p (cal/gm-°C)	Temperature (°C)	Reference No.
0.258	-167.57	3
0.431	- 80.32	3
0.364	0.00	33

8. THERMODYNAMIC PROPERTIES:

Quantity	Reference No.
$H_{f,298} = -66.66$ kcal/gmole	32
$H_{f,298} = -74.50$ kcal/gmole	28
$H_{\text{comb.}} = -1062.1$ kcal/gmole	28
$F_{f,298} = -37.71$ kcal/gmole	32

9. VAPOR PRESSURE: (Reference No. 21)

P (mm Hg)	1	10	40	100	400	760
Temp. (°C)	12.0	43.0	66.3	84.0	125.5	155.0

10. SOLUBILITY IN WATER: (Reference No. 29)

0.124 gms./100 gram solution @ 11.4°C