THE EFFECT OF ULTRASONIC ENERGY
ON THE PYROLYSIS OF n-BUTANE

By

ARNOLD HARVEY PELOFSKY

Bachelor of Science
Brooklyn College
Brooklyn, New York
1955

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1963

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
May, 1971

THE EFFECT OF ULTRASONIC ENERGY
ON THE PYROLYSIS OF n-BUTANE

Thesis Approved:

John H Erbar
Thesis Adviser

Billy L Crynes

John B West

Kenneth J Bell

Robert D Morrison

D D Durham
Dean of the Graduate College

PREFACE

This dissertation concerns the effect of ultrasonic energy on the pyrolysis of n-butane. Experimental data were gathered and a statistical model was derived that proves that ultrasonic energy has a positive effect on the pyrolysis process. Ultrasonic energy facilitates pyrolysis not only by producing additional product but also reducing the reaction time significantly.

I would like to take this opportunity to express my appreciation to Professor John H. Erbar for the assistance and guidance given me; to the Frank J. Seiler Laboratory, Air Force Adacemy, Colorado, for the use of their laboratory facilities and their computer; to Phillips Petroleum Company, Bartlesville, Oklahoma, for a generous supply of n-butane; and to Monsanto Corporation, Texas City, Texas for chromatographic standards.

In addition, I would like to especially thank Cities Service Oil Company, Tulsa, Oklahoma, for their financial support as well as their interest; and to thank Mary Beth Milligan for her typing excellence and advice.

Finally, I would like to express my deepest appreciation to my wife, Loretta, and to my two children, Deborah and Michaela, whose understanding, encouragement, and sacrifice were instrumental in the preparation of this dissertation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

STATEMENT OF PROBLEM

With the passing of every year, there seems to be an increased market for petroleum products. In 1970, the demand reached 14.8 million barrels per day. It is anticipated that there will be at least a 5% increase in demand in the years ahead (38). Because of this increase, there will be a shortage of propylene and ethylene by 1975 if newer ways of producing these substances are not found and exploited (36).

Propylene consumption for petrochemicals has grown from 1 billion pounds in 1950 to 5.9 billion pounds per year in 1966. Expected future growth should require 14 - 16 billion pounds by 1975. Propylene is primarily used today for alkylate for the gasoline market. Gasoline consumes 70 percent of the propylene produced. This rate is expected to drop to 55 percent by 1975, but the overall amount of propylene consumed will rise (18). Gasoline volume has risen from 4.7 million barrels per day in 1966 to 5.6 million barrels per day in 1970 (19). This rise in gasoline volume should continue through the 1970's.

Consumption of ethylene is expected to increase at the rate of 9 percent annually between 1970 and 1975, thereby resulting in a demand of 29 billion pounds in 1975 compared with 9.35 billion pounds in 1965. Polyethylene will continue to be the largest single consumer of ethylene. Other major markets for ethylene are ethylene oxide, ethanol, styrene monomer, and vinyl chloride monomer. The continued growth of these established markets in addition to the new uses ensures a solid market growth for ethylene (32).

Normal-butane is available in both natural gas and crude petroleum. At present, a large percentage of n-butane is isomerized to isobutane for alkylation. N-butane could also be used to help make up the deficit of propylene and ethylene. The deficit exists because propylene is produced as a byproduct from catalytic cracking and ethylene manufacture. As the use of zeolitic cracking catalysts increase, less propylene is produced than when silica alumina catalysts are used. To increase ethylene production with present fixed capacity requires higher severity with a heavy feedstock or shifting the feedstock from propane to ethane (36).

At present, normal butane is used as an ethylene-plant feedstock in relatively few commercial installations. From the standpoint of maximum utilization of feedstock, it is advantageous to crack normal butane at high conversion per pass because any unconverted normal butane will contaminate the butadiene and butene streams thereby incurring additional expense for separation of the components (40).

This study was undertaken to demonstrate the technical feasibility of cracking n-butane in an ultrasonic field and to study the kinetics of decomposition. Ultrasonic energy, used in a proper fashion, will increase the conversion of hydrocarbon feedstocks. Up to the present, virtually no work has been done on investigating the effect of ultrasonic energy on a gas-phase thermal cracking process. Therefore, a method was devised to test the hypothesis that ultrasonic energy will affect the pyrolysis process and, at the same time, study the kinetics of pyrolysis. In order to study the kinetics with a minimum of secondary reactions, it was necessary to keep conversion low. N-butane was selected because it is readily available and has a relatively simple structure. A detailed statistical analysis was performed to help interpret the experimental data.

CHAPTER II

RELATED LITERATURE

General Applications

The application of ultrasonic energy has been suggested for many varied uses. Bobkiewicz (3) suggested that ultrasonic energy in one form or another can be used to:

a) Remove soot from chimneys;
b) Produce H_2SO_4 mist;
c) Remove alkali salts from exhaust gases;
d) Clean metallic and optical surfaces;
e) Prevent scale deposits in steam boilers;
f) Produce stable emulsions;
g) Drill holes;
h) Control the quality of various products;
i) Wash textiles.

Rozycka (25) suggested that ultrasonic energy enhances many chemical reactions; such as:

a) Polymerization;
b) Depolymerization;
c) Electrolysis;

and physical reactions such as:

a) Separation of gases;
b) Crystallization;

c) Extraction;
d) Distillation;
e) Emulsification;
f) Coagulation;
g) Dispersion of solids in liquids;
h) Filtration;
i) Aerosol formation.

Mechanism

Nosov (17) postulates that all of the above applications are the result of cavitation. When a liquid is subjected to ultrasonic waves, one can usually observe or detect the formation of small bubbles in the liquid. Cavitation is usually the term used to describe the formation and the "activity" of these bubbles. The cavitation process may be divided into three stages: nucleation or initiation, growth, and finally, catastrophic collapse. Usually, initiation occurs either from submicroscopic impurities and voids or from "weak spots" in the liquid itself. During the rarefaction phase of the ultrasonic wave, the void expands and the bubble begins to grow. As the bubble cavity expands, the surrounding liquid evaporates into the cavity. The bubble may reach a size ranging from 10^{-4} to 10^{-5} cm (8). In the catastrophic collapse, the condensation phase of the ultrasonic wave pushes the walls of the bubble inward to a diameter of the order of 10^{-6} to 10^{-5} cm. As a result, the contents of the bubble are highly compressed, and it is estimated that very high instantaneous temperatures (10,000°F) and pressures (75,000 psi) can occur (10).

History

Historically, Einstein (6) was the first investigator to suggest that ultrasonic energy might affect a chemical reaction. He investigated the effect of ultrasonic energy on the chemical equilibrium of the $N_2O_4 \rightleftarrows 2NO_2$ reaction. He observed that the system absorbed sound energy thereby shifting the equilibrium of the reaction. On the basis of these results, other investigators started examining ultrasonic energy.

Szent-Gyorgi (33), in 1933, was the first to observe that an organic material would react if the material was irradiated with ultrasonic energy. He observed that sonic irradiation of an aqueous solution of carbohydrate produced a variety of dextrins. Since then much work has been done in this area. Schmid (29) found that sonic irradiation of a high molecular weight polymer solution yielded a solution with a lower molecular weight. He postulated that the depolymerization of the polymer was the result of the friction between the molecules of the solvent and the solute.

In 1944, Ilibontry (14) investigated the effect of ultrasonic energy on aromatics. He observed the decomposition of benzene in an aqueous solution. Prudhomme et al (22), in 1947, observed that benzoic acid, phenol, indole, quinine, thymine, and barbituric acid in an aqueous solution also decompose under the influence of ultrasonic energy. Weissler et al (37) reported that, under the influence of ultrasonic energy, he was able to react carbon tetrachloride with water. He postulated that this reaction was possible because the collapse of the bubbles resulting from cavitation, generated electrical forces which caused the reaction to occur. This reaction does not proceed in the absence of ultrasonic energy. Siegel (30) in 1958 showed that cysteine could be oxidized to cystine under the influence of an ultrasonic field. This reaction occurred only if tellurium ions and ultrasonic energy were present. The tellurium acted as a reducing agent. Rozycka (25), in 1965, reported the production of hydrogen cyanide from methane and nitrogen when the mixture was irradiated with sonic energy. This reaction was especially noteworthy since it is an endothermic reaction and not thermodynamically spontaneous. Temperatures greater than 500°C and pressures greater than 100 atmospheres would be necessary to react nitrogen and methane in a conventional manner.

Process Applications

Several investigators have applied sonic energy to industrial processes. Coffin and Funt (5), in 1959, studied the effect of sonic energy on fractional distillation. They replaced the bubble cap trays in a distillation tower with ultrasonic transducers.

Greguess (11), in 1956, reported the cyclization and aromatization of n-hexane in the presence of ultrasonic energy. Parthasarathy et al (20), in 1962, demonstrated the esterification of ethyl alcohol when the liquid was sonically irradiated. Balakishiev et al (1,2), reported in 1962 and again in 1965 that ultrasonic energy influences the quality and quantity of gasoline from cracking a high molecular weight crude oil. They showed that the yield of the gasoline increased with an increase in ultrasonic intensity and temperature. The amount of high molecular weight paraffins in the gasoline decreased, the amount of naphthenic hydrocarbons remained unchanged, and the amount of hydrogen produced decreased. They further demonstrated that the increase in ultrasonic intensity produced the same effect as an increase in temperature with other conditions being similar.

Theory

Several authors have suggested possible theories as to how the above processes proceed. The theory most commonly accepted involves cavitation with the resulting collapse of bubbles in which the reaction takes place.

Figure 1 (9) shows a comparison of the collapse curves for cavities in which either an exothermic reaction or an endothermic reaction or no reaction takes place during the bubble's collapse. As can be seen from this figure, the cavity containing the gas in which an exothermic reaction is taking place requires a longer time to reach the same radius in the final stages of collapse than the cavity in which no reaction is taking place. This results from the fact that energy is released by the reacting gases in addition to the energy from the adiabatic compression of the gas in the cavity. The gas temperature and pressure will increase thereby retarding the collapse of the bubble to a greater extent than the collapse of the bubble without reaction. It is also noted that the radius on collapse is greater for the exothermic case. When the reaction is endothermic, the compression energy is absorbed by reaction, resulting in a lower gas temperature and pressure. Therefore, the gas offers less resistance to collapse than in the non-reacting case. The time required to reach a given radius is less in the endothermic case than in either the exothermic or the non-reacting cases (9).

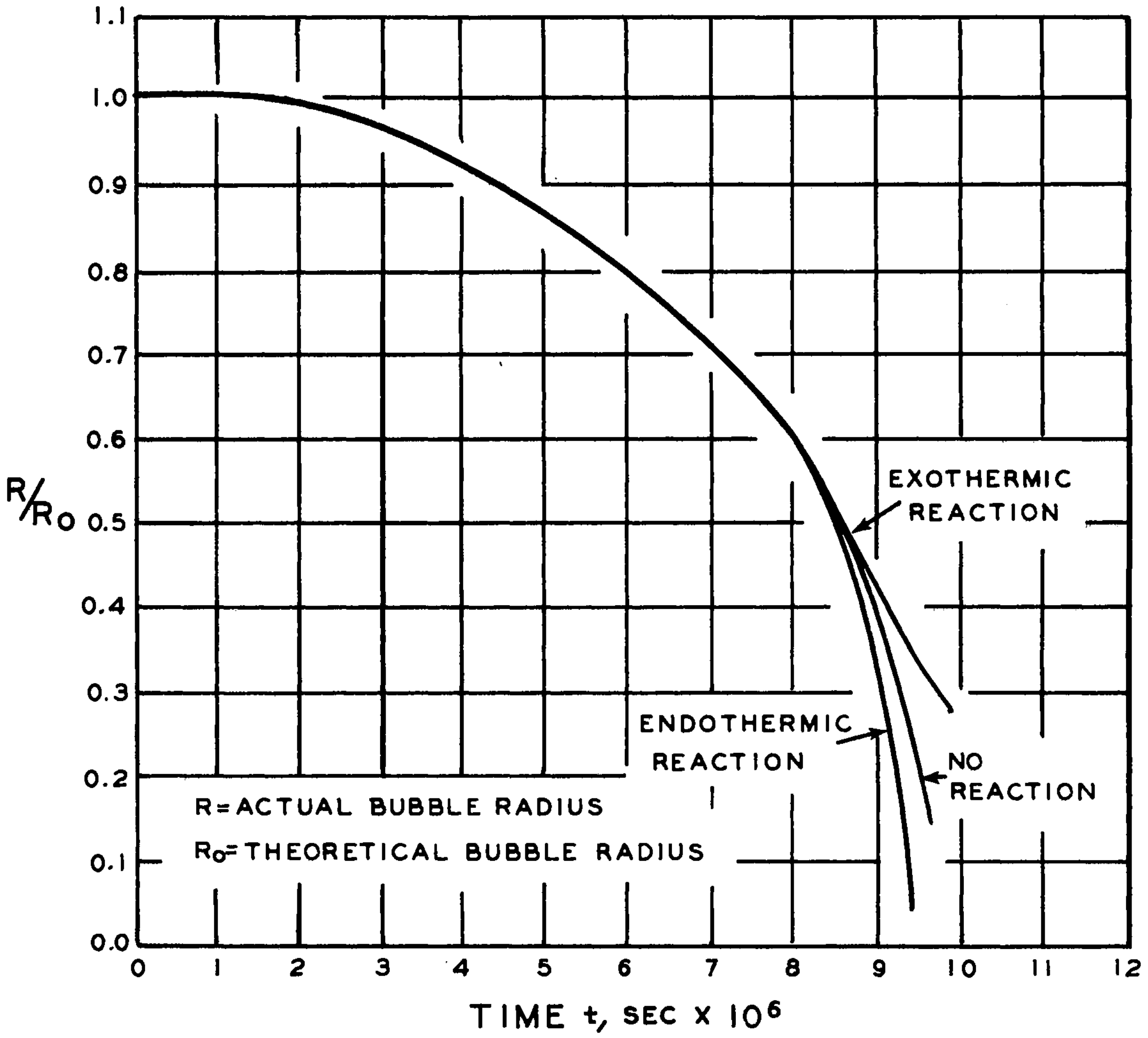

FIGURE I COLLAPSE CURVES OF A BUBBLE CAVITY RESULTING FROM CAVITATION

Very little has been found in the literature to suggest that previous studies have been made to determine the effect of ultrasonic energy on the pyrolysis of hydrocarbons. Balakishiev's (1,2) work seems to be the only comprehensive one in this area. However, previous to his work, authors have noted similarities between the thermal decomposition of hydrocarbons and the decomposition of hydrocarbons by other types of radiation such as x-ray and nuclear radiations.

Haissinsky et al (12), in 1950, postulated that ultrasonic energy will behave as x-rays or α-rays in promoting decomposition of a material. He believed that a free radical mechanism such as proposed by Steacie (31), applies in all cases. Lindstom (15) drew the same analogy. Both Brodskii (4) and Schenck (28) came to the same conclusions with respect to decomposing petroleum fractions and methane respectively.

Though the above investigators have intimated that the introduction of sonic energy may actually facilitate and accelerate the thermal decomposition of hydrocarbons, virtually no work has been done in this area. The pyrolysis of a hydrocarbon in a homogeneous gas phase system has also not been investigated probably because of the inefficiency of introducing ultrasonic energy into the system. However, Lynnworth (16) suggested a method for increasing efficiency by incorporating a resonant water layer to increase the transmission of the sonic energy. He indicates that a resonant water layer will produce a transmission gain of 11 dB.

Kinetics of n-Butane Decomposition

The study of the decomposition of n-butane in the gaseous phase has been studied by several investigators. In 1931, Rice (24) proposed a free radical mechanism for the reaction. It was substantiated by Purnell and Quinn (23) in 1962, and by Sagert and Laidler (26) in 1963. In essence, all showed the following decomposition mechanism:

$$C_4H_{10} \rightleftarrows 2C_2H_5\cdot \qquad (1)$$

$$C_2H_5\cdot + C_4H_{10} \rightleftarrows C_2H_6 + C_4H_9\cdot \qquad (2)$$

$$C_4H_9\cdot \rightleftarrows CH_3\cdot + C_3H_6 \qquad (3)$$

$$C_4H_9\cdot \rightleftarrows C_2H_5\cdot + C_2H_4 \qquad (4)$$

$$CH_3\cdot + C_4H_{10} \rightleftarrows CH_4 + C_4H_9\cdot \qquad (5)$$

$$C_2H_5\cdot \rightleftarrows C_2H_4 + H\cdot \qquad (6)$$

$$H\cdot + C_4H_{10} \rightleftarrows H_2 + C_4H_9\cdot \qquad (7)$$

$$2C_2H_5\cdot \rightleftarrows C_2H_4 + C_2H_6 \qquad (8)$$

Parnell and Quinn (23) postulated this mechanism by correlating the results of eleven hundred experimental runs. "Clean Pyrex" vessels were used as their reaction chambers since the vessel may act as a catalyst for the reaction. All of their experimental runs were carried out in a batch (static) system. Pyrex vessels were selected because it was assumed that the pyrex material was inert. The major products of the decomposition were hydrogen, methane, ethane, ethylene and propylene.

They further reported that:

a) No propane was ever found in the products of the pyrolysis of n-butane alone.

b) The rate of formation of each major product was at a maximum at the start of each reaction.

c) The distribution of the major products was independent of the extent of the reaction at any initial pressure and temperature.

d) The yields of methane and propylene were identical and considerable differences between the yields of ethane and ethylene were common.

N-butane was pyrolyzed over a temperature range of 420 to 530°C at initial pressures between 10 and 150 mm Hg. Approximately 10% of the n-butane was decomposed. They reported that the rate of disappearance of n-butane can be correlated to:

$$\frac{-d\ (C_4H_{10})}{dt} = 3.8 \times 10^{14} \quad \exp\left(\frac{-58{,}300}{RT}\right) (C_4H_{10})^{1.5} \qquad (9)$$

$$cc^{1/2} mole^{-1/2} sec^{-1}$$

Sagert and Laidler (26) studied the pyrolysis of n-butane in the temperature range from 520 to 590°C and at pressures from 30 to 600 mm Hg. They reported that the rate of decomposition of n-butane can be correlated with the following empirical equation:

$$-d\ \frac{(C_4H_{10})}{dt} = 3.24 \times 10^{15} \quad \exp\left(\frac{-59{,}900}{RT}\right)(C_4H_{10})^{1.5} \qquad (10)$$

$$cc^{1/2} mole^{-1/2}\ sec^{-1}$$

Equations (9) and (10) both indicate an order of 1.5 for the decomposition of n-butane, however, the frequency factor varies by a factor of 10 between the equations. This difference between the preexponential factor (usually called the frequency factor) can probably be explained by the fact that the reaction chambers were made of different materials. Sagert and Laidler used quartz vessels and thermally decomposed 15% of the n-butane into products. Both sets of investigators acknowledge that the reaction of pyrolyzing n-butane is sensitive to the surface of the reaction vessel.

Wang et al (35), and Sandler and Lanewala (27) studied the thermal decomposition of n-butane under flow conditions and low conversion levels (0.05-5%). Both agreed on a Rice-type, free-radical mechanism presented earlier, but they disagreed on the order of the reaction. Wang felt that the reaction order was between one and two while Sandler felt the reaction was essentially first order. Both investigators studied the reaction at a pressure of one atmosphere, but Wang operated over a temperature range of 460° to 560°C while Sandler operated in a temperature range of 427° to 726°C.

Wang correlated his results to the following equations:

for first-order reaction:

$$-\frac{d\,(C_4H_{10})}{dt} = 3.34 \times 10^{12} \exp\left(\frac{-54{,}600}{RT}\right)(C_4H_{10}) \qquad \text{sec}^{-1} \qquad (11)$$

for second order reaction:

$$-\frac{d\,(C_4H_{10})}{dt} = 2.55 \times 10^{14} \exp\left(\frac{-56{,}800}{RT}\right)(C_4H_{10})^2 \quad \text{ft}^3/\text{lb sec} \qquad (12)$$

(To convert to g-moles/cc sec, multiply frequency factor by 2.76 x 10^{-4}. The units refer to the rate constant.)

Sandler and Lanewala (27) suggested a temperature dependency to the frequency factor. They published the following equations:

Temp Range (°C)	Equation
427 - 521	$-\frac{d\,(C_4H_{10})}{dt} = 0.8 \times 10^{10} \exp\left(\frac{-46{,}000}{RT}\right) C_4H_{10}$ sec^{-1} (13)
521 - 611	$-\frac{d\,(C_4H_{10})}{dt} = 13.7 \times 10^{10} \exp\left(\frac{-52{,}000}{RT}\right) C_4H_{10}$ sec^{-1} (14)
611 - 726	$-\frac{d\,(C_4H_{10})}{dt} = 19.5 \times 10^{10} \exp\left(\frac{-54{,}000}{RT}\right) C_4H_{10}$ sec^{-1} (15)

The difference in the results of these investigators can also probably be explained by the nature of the material used to fabricate the reaction vessel. Wang used a stainless steel reaction chamber while Sandler used Vicor, 97% silica material, in his reaction chamber.

Torok and Sandler (34) also studied the thermal decomposition of n-butane. Their work, in the temperature range of 330 to 420°C, indicated that the reaction order was both temperature and pressure dependent when the reaction order approached 0.5.

All the investigators demonstrate reproducible results, however, there seem to be glaring inconsistencies between the results of each. The one notable difference, of course, is that each used a different material for his reaction chamber. If nothing else, this does illustrate the importance of the materials of construction when studying this reaction. The dependency on the reactor material is more pronounced in the numerical value of the frequency factor than in the numerical value of the activation energy.

No indication was found in the literature of the study on the effect of ultrasonic energy on the pyrolysis of n-butane. The objective of this experimental study is to provide these data.

Statistical Treatment

In order to determine the effect of ultrasonic energy on the pyrolysis of n-butane, an experimental design was used that compared the experimental data when ultrasonic and heat energy were used (Group C) to the experimental data when only heat energy was used (Group B). Both of these groups were compared to a "control" group (Group A). The control group was not exposed to either heat or ultrasonic energy. The data were gathered on the control group because of the normal experimental variation in the analytical data.

The preferable method would be to evaluate the effect of ultrasonic energy on solely a chemical kinetic foundation, but, because technical grade n-butane (99% purity) was used, a statistical evaluation of the effect of ultrasonic energy was necessary. The impurities in the n-butane feed along with the low conversion levels of n-butane in the experimental runs tended to obscure the true chemical kinetic picture. Since the objective of this experiment was to demonstrate either a positive or negative effect of ultrasonic energy, a statistical treatment was sufficient.

The experimental data were subjected to the following statisical treatment:

a) t-test;

b) Analysis of Covariance;

c) Stepwise Regression Analysis.

The measure t is a ratio of the difference between the averages of the groups to the standard deviation of this difference. The quantity t is a measure of confidence in the result. The larger the observed difference, the smaller the standard deviation, and the more measurements that are available, the greater will be the weight attached to the conclusion that there is a difference between the groups. If there are more than thirty experimental observations, the t-test will reliably indicate a significant difference between the groups if, indeed, a difference exists.

Analysis of covariance is a combination of analysis of variance and regression analysis. The analysis of covariance is used when experimental conditions existing for each group cannot be made the same. The precision of an experiment may be greatly increased by equalizing, among the treatment groups, potential sources of error such as differences in temperature, pressure, and reaction time. These sources of error are eliminated from the comparisons by mathematically subtracting the effect in the regression model and, by the analysis of variance, equally eliminated from the estimate of error. The predicted values from the regression model are then compared using the F-test. The F-test determines whether the variance found between the groups differ significantly from the variance found within each group.

Regression analysis is a particular statistical procedure which is used to "curve-fit" the experimental data. Stepwise regression tests each significant variable independently. The equation is derived by considering only the significant variables. If the variable does not offer significance to the regression equation, it is deleted from consideration.

The analysis of covariance was computed using the BMD 04V program, Seiler laboratory modified version dated September 17, 1965. The stepwise regression analysis was computed using the BMD 02R program, July 17, 1966 version that was modified for the Seiler laboratory by the UCLA Health Science Computing Facility. These programs were run on the Burroughs B5500 computer.

CHAPTER III

METHOD AND PROCEDURE

The effect of ultrasonic energy on the pyrolysis of n-butane was investigated by dividing the experiment into three parts. The first part consisted of accumulating data on a control group (A) to which no treatment was applied. The second part consisted of accumulating data when only heat energy was applied (Group B). The third part consisted of accumulating data when heat and ultrasonic energy were applied (Group C). In each of the last two parts, the reaction time and the sample size (weight of the gas and its pressure) were varied randomly. The data on all parts were accumulated alternately, i.e., first a control run was made, then heat energy was introduced to another gas sample for a specific time, then heat and ultrasonic energy were applied to another gas sample for a specific time. The analytical data from all parts were correlated and compared statistically.

Equipment

Reaction Chamber

The gas was introduced into a reaction chamber fabricated by Automation Industries Inc., Boulder, Colorado. The reaction chamber consisted of a stainless steel cylinder with a diameter of 2.5 inches, a length of 4 inches and a thickness of 0.5 inches (Figure 2). A 2 inch diameter ceramic barium titanate (Curie point 300°C) ultrasonic transducer was fitted snugly against the inside wall of the reaction chamber (Figures 3a and 3b). Electrical connections were attached to the transducer with a high temperature inert epoxy. These leads were passed through the wall of the reaction chamber using connections coated with a non-conducting ceramic material in a stainless steel sleeve. The stainless steel sleeves were then silver soldered into holes drilled through the top of the chamber. A 300 psi vacuum/pressure gauge was silver soldered on the top of the chamber. The gauge was Model Number R-12 manufactured by Marsch Instrument Company, Skokie, Illinois. A .25 inch inlet stainless steel needle valve manufactured by Lunkenheimer, Cincinnati, Ohio and a .25 inch outlet stainless steel needle valve manufactured by Whitey Research Tool Company, Emeryville, California were silver soldered in place. The valves were positioned 0.75 inches from the top of the chamber and soldered in place. A removable stainless steel cap 0.5 inches thick was the bottom of the chamber. A neoprene gasket was used between the inner surface of the cap and the chamber walls to assure a gas tight connection. Connections to the heating element and to two chromel-alumel thermocouples were installed within the cap (Figures 4a and 4b). The heating element was located 1.5 inches from the top of the chamber and consisted of a 10 inch length of 22 mil Nichrome wire coiled around a 0.25 inch diameter ceramic cylinder 2 inch in length. The junction of the thermocouples was positioned perpendicular to the heating element, equidistant between the cylinder wall and the thermocouple, and 0.5 inches above the heating element.

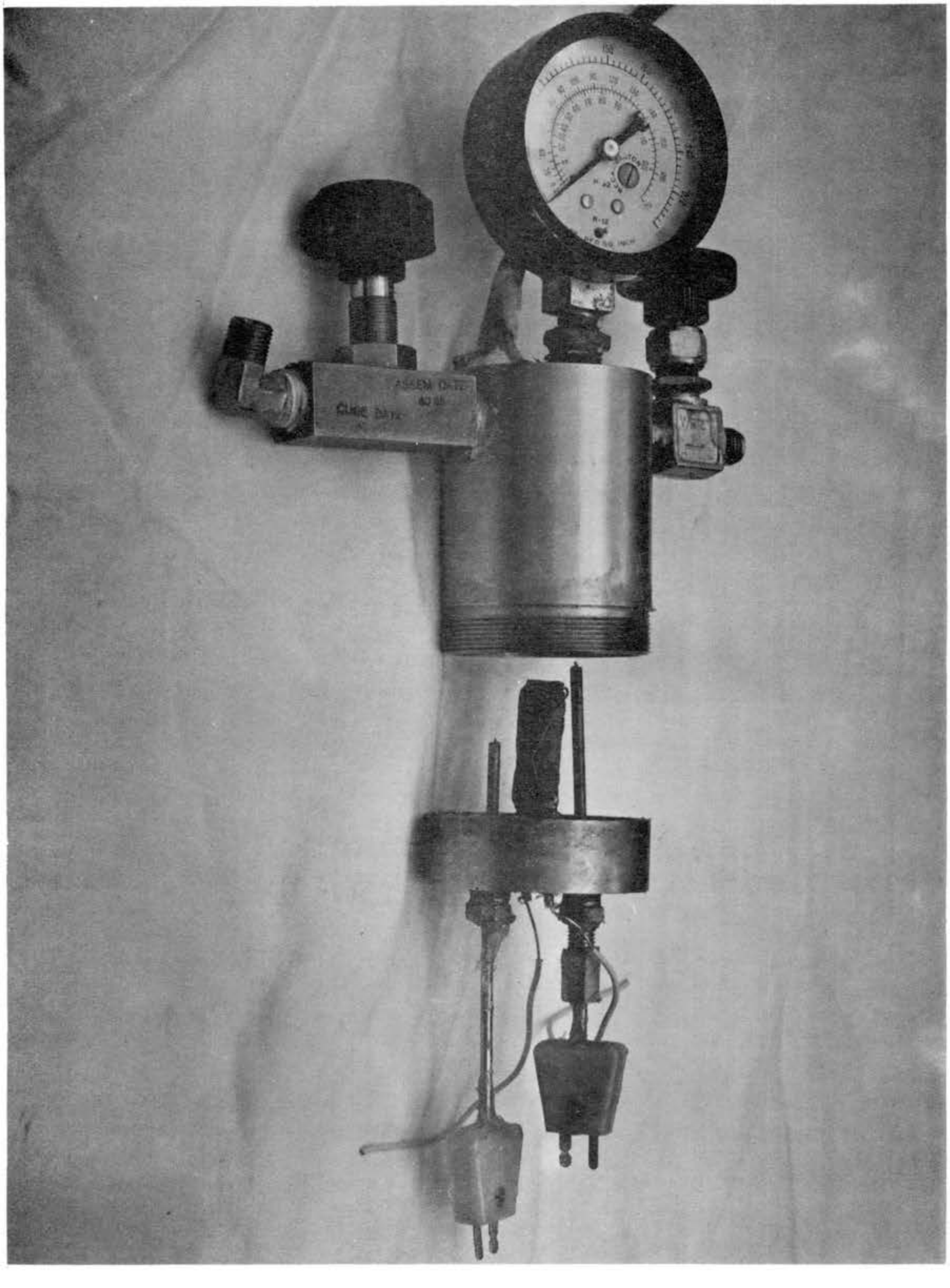

FIGURE 2 REACTION CHAMBER AND CAP

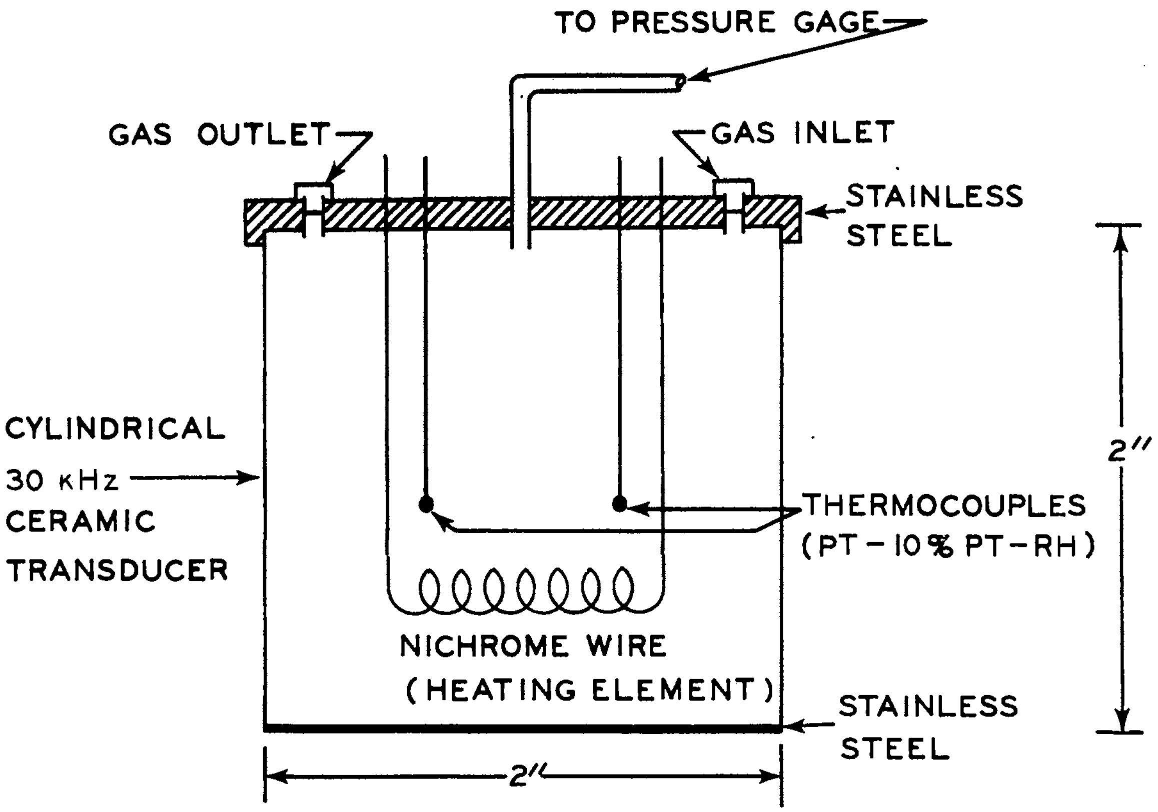

FIGURE 3a REACTION CHAMBER SCHEMATIC

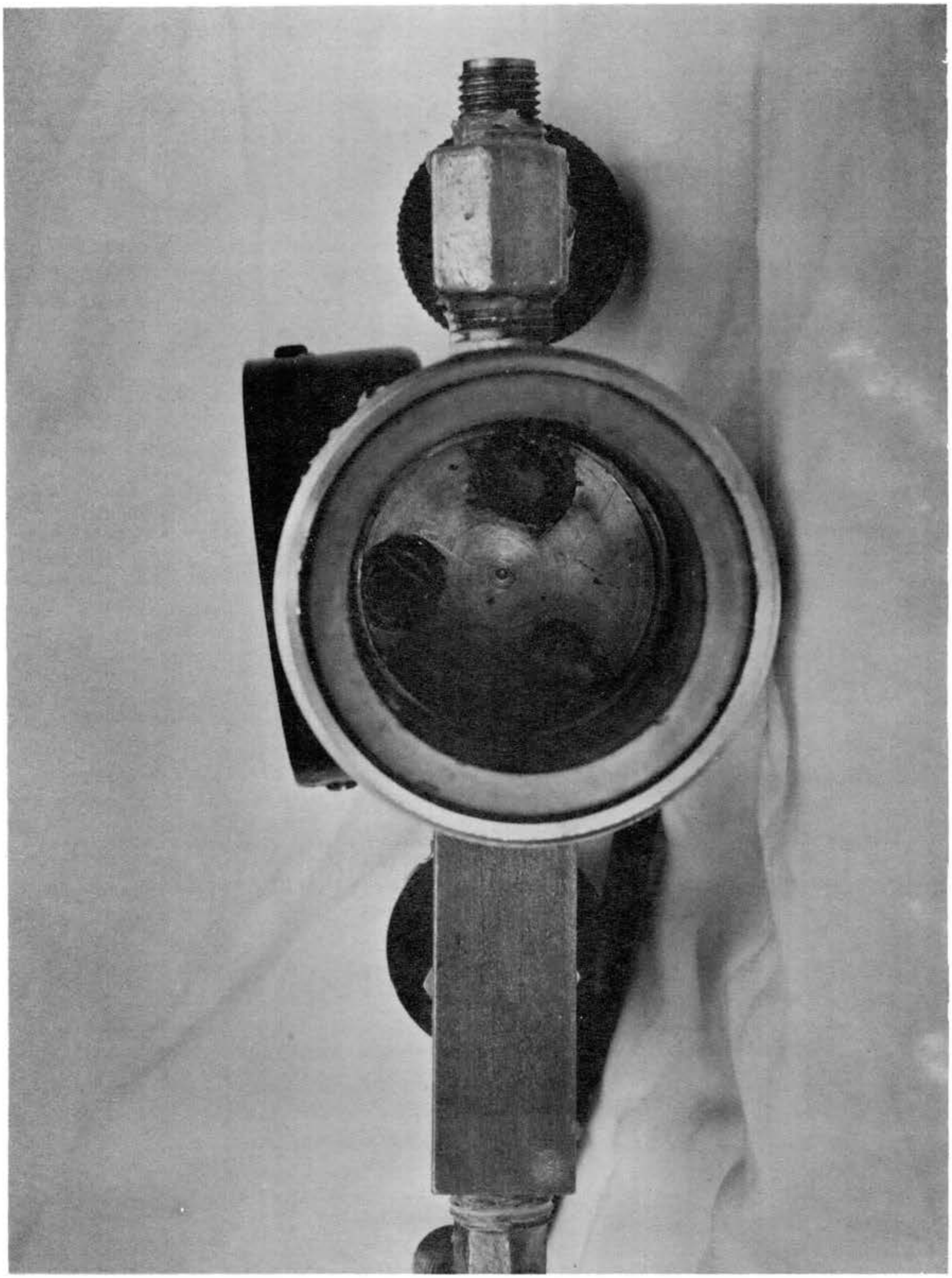

FIGURE 3b REACTION CHAMBER

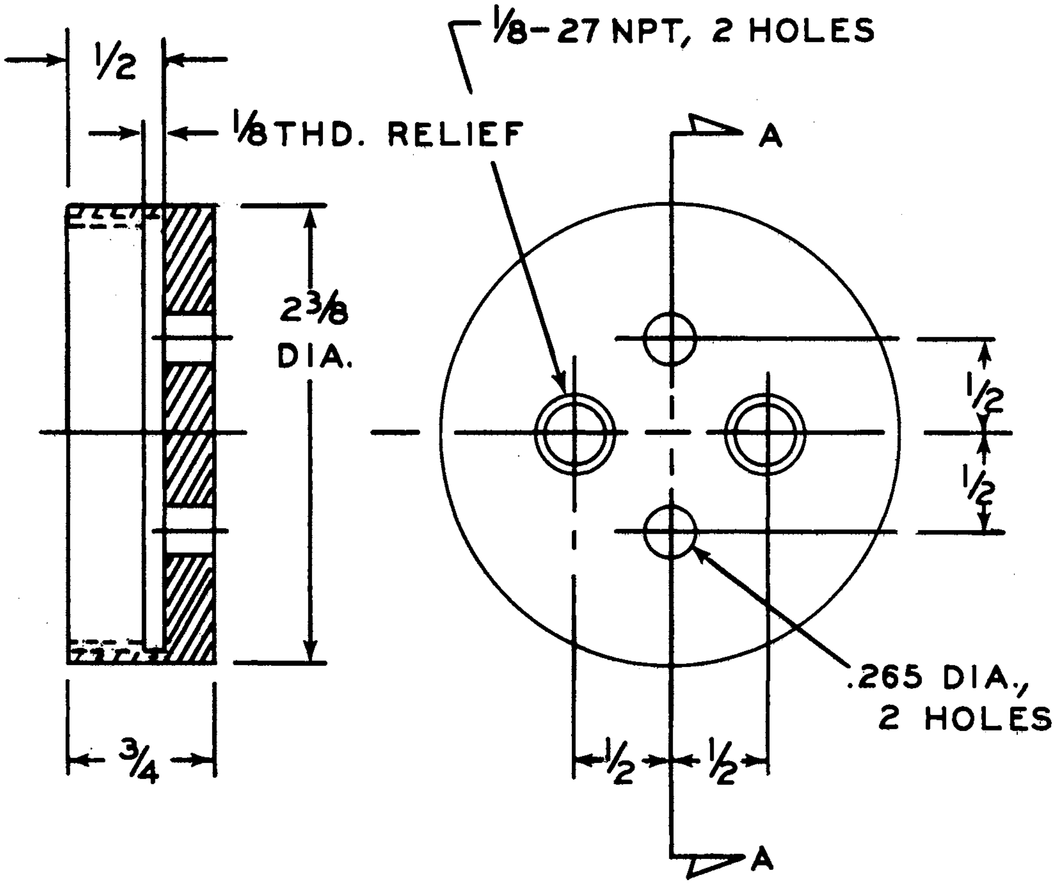

FIGURE 4a REACTION CHAMBER CAP

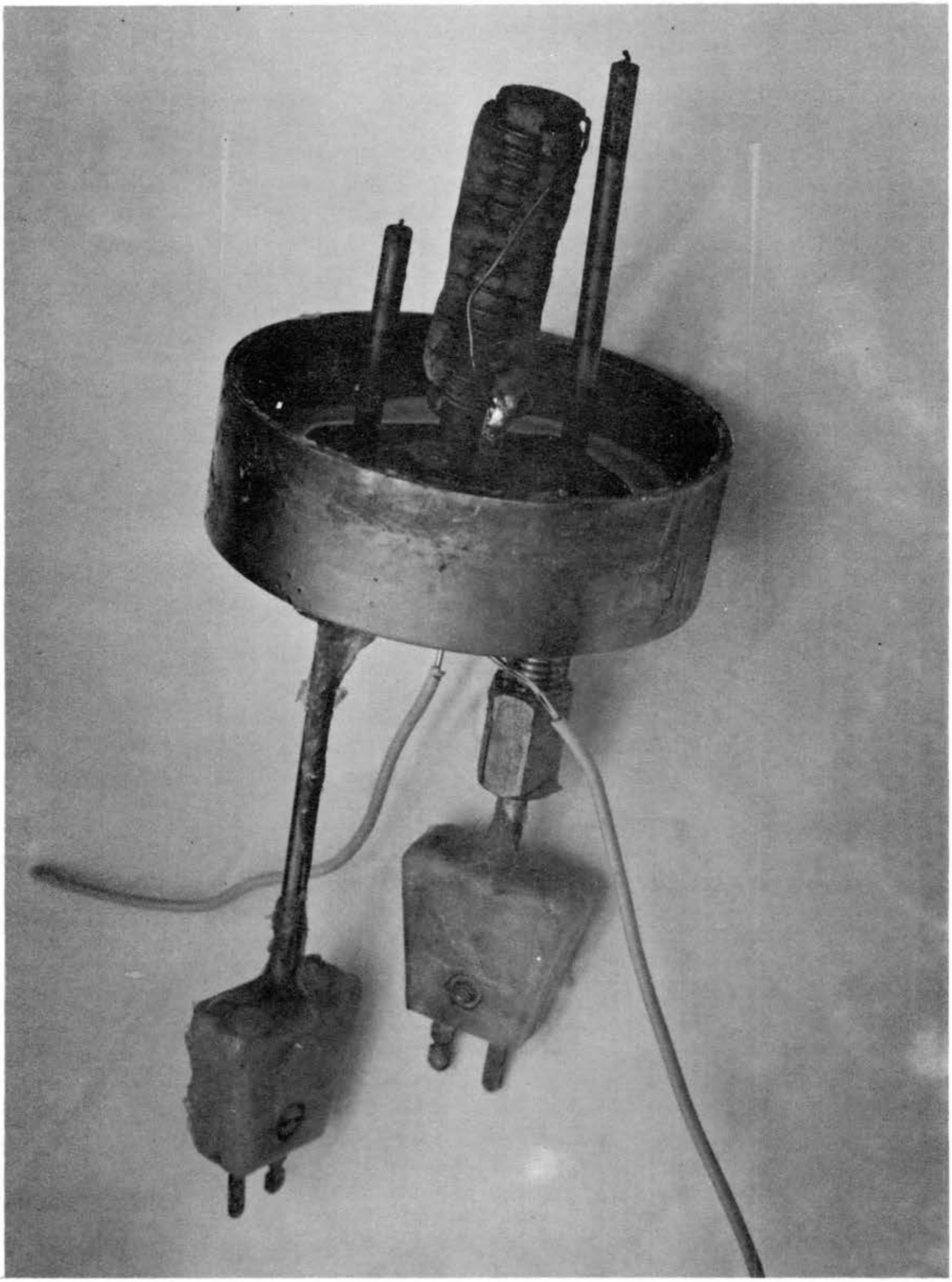

FIGURE 4b REACTION CHAMBER CAP

Heating Element

The heating element was activated by applying voltage to it with a 130 volt, 7.5 amperes variable voltage transformer, Model No. 116 manufactured by The Superior Electric Company, Bristol, Connecticut. A 1-10 amperes alternating current ammeter, Model No. 850, manufactured by Shurite Meters Inc., New Haven, Connecticut was placed in series in the line. Throughout the study the voltage was kept at 10.9 volts and the current at 4.5 amperes. At steady state, the temperature of the coil was 400°C at nonreacting conditions. This temperature was measured with an optical pyrometer, Model No. 81F, manufactured by Pyrometer Instrument Inc., Bergenfield, New Jersey. That portion of the heating element facing the thermocouples was coated with a ceramic cement.

Thermocouples

The thermocouples were manufactured by Omega Thermocouples Inc., Stamford, Connecticut. The thermocouple wire was 0.01 inches in diameter and sheathed with a leakproof ceramic coating. The ceramic coating was jacketed by 316 stainless steel. Only the thermocouple junction was exposed to the reaction. The calibration of the thermocouples was evaluated by using a heated oil bath over the reactions temperature range and found to be ± 1C° of the published calibration charts. The temperature of the heated oil bath was measured with a N. B. S. calibrated thermocouple. Each thermocouple had its own strip chart recorder. These recorders were 6 inch Azar Model 300 strip chart recorders manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania.

Ultrasonic Generator

The activating source for the ultrasonic transducer was an Ultrasonic Generator, Model No. 1049, designed and fabricated by Automation Industries, Boulder, Colorado (Figure 5). The power and frequency output of this generator could be varied. The generator was set at its maximum power output (500 watts). The frequency was set to the resonating frequency of the transducer. The resonating frequency was found by tuning the generator until maximum plate current was obtained. The transducer was a piezoelectric device which converted electrical energy to mechanical vibrational energy. The transducer resonated in a frequency range of 27.5 to 29.0 kHz with the average of 28.3 kHz for a particular experimental run.

Gas Chromatography

The gas samples were analyzed using a GC-4 Gas Chromatograph manufactured by Beckman Instruments Inc., Fullerton, California. The Chromatograph was equipped with a dual hydrogen flame detector. A 20 foot, 1/8 inch I. D. copper column filled with a 20% mixture of hexamethylphosphoramide liquid supported on 80 - 100 mesh Chromosorb P was used. The temperature of the column was kept at 0°C by inserting it into a water bath containing ice. Helium was used as the carrier gas, and its inlet flow rate was 25 cc/min. In order to achieve maximum sensitivity and still have a low noise ratio, it was necessary to have a air flow rate of 200 cc/min., a hydrogen flow rate of 45 cc/min. and a helium flow rate of 105 cc/min. to the hydrogen flame. In order to obtain the high helium flow rate, an additional 80 cc/min. was added

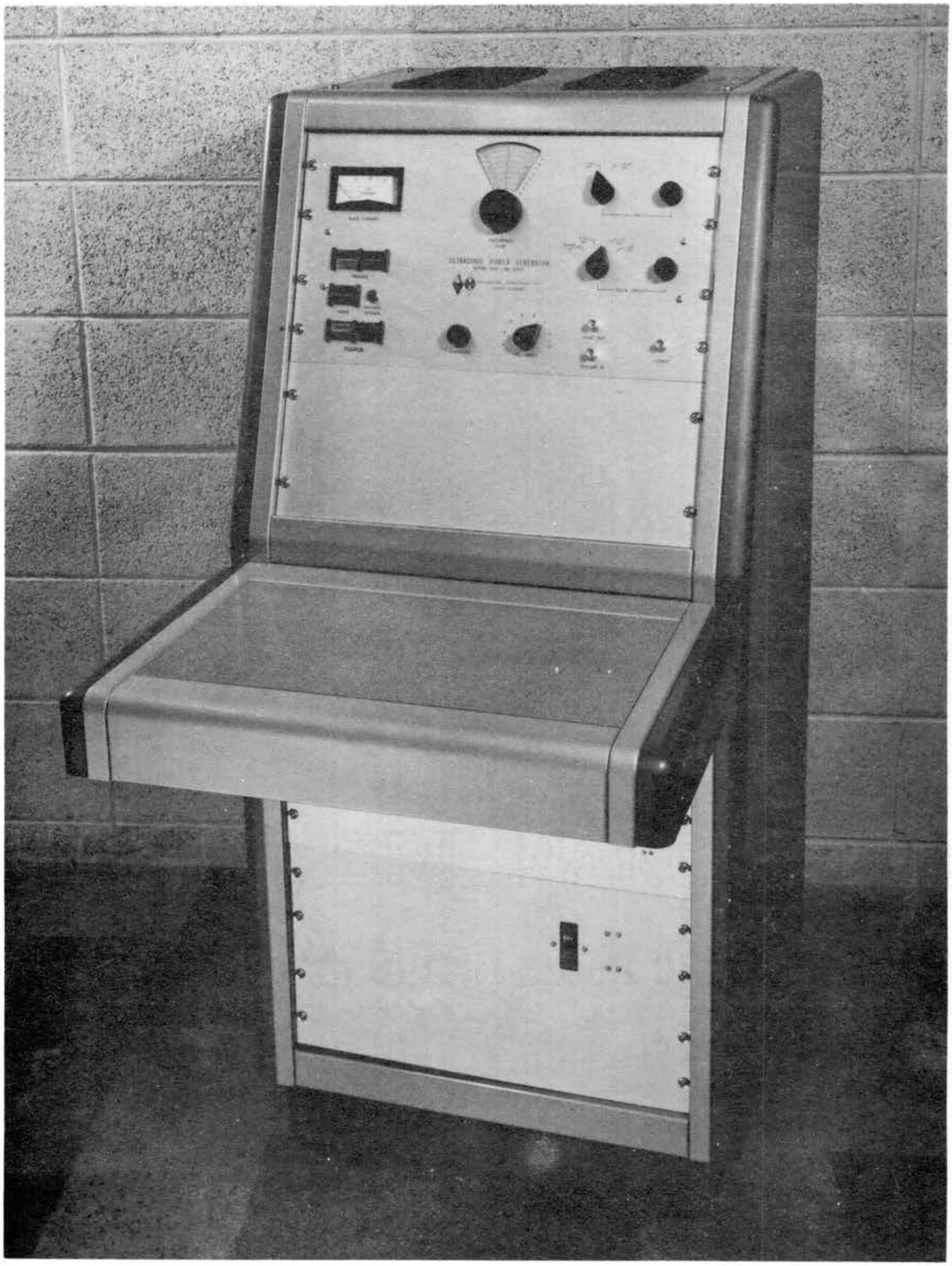

FIGURE 5 ULTRASONIC POWER SUPPLY

at the column outlet so that the total flow rate to the detector would be 105 cc/min. These flow rates were continually checked using Matheson rotameters. These rotameters were installed as a part of the GC-4 instrument. They were calibrated using a soap bubble flowmeter. These flow rates to the detector substantially decreased the external and internal noise level so that it was possible to detect a current of 10^{-12} amperes with the Beckman electrometer which was in line with the dual flame hydrogen detector and the recording instrumentation. With this sensitivity, parts per billion of trace components could be detected.

Analytical Procedure

The G. C. response curves were recorded on a Beckman 10 inch linear recorder, catalog number 100500. The curves were integrated using a direct metric reading Compensating Polar Planimeter, No. 62-0005, manufactured by K&E Inc., Hoboken, New Jersey. Table I is a compilation of the average of the chromatographic data for the feedstock. The concentration of n-butane was standardized to a known concentration supplied by Monsanto Corporation, Houston, Texas. The concentration of the other components could not be calibrated because no supplier could furnish ultrapure components. Furthermore, it was not possible to completely separate the C_2 and C_3 olefins from the C_2 and C_3 paraffins respectively. Of course, it would have been more desirable to calibrate each component, but since this procedure was not possible a simple normalization method was used.

TABLE I

CHROMATOGRAPHIC DATA CALIBRATION

Component	Composition (Relative Wt. %)	Chart (Inches)	Time (min)	Attenuation	Amps x 10^{12}
Methane	.0003	17.95	1.795	5	2.5
Ethane	.0001	22.53	2.253	5	2.5
Propylene	.0102	37.45	3.745	2×10^2	100
Propane	.0024	48.21	4.821	50	25
Isobutane	.3585	65.78	6.478	1×10^3	500
n-Butane	99.5915	92.58	9.253	1×10^5	50,000
1-Butene	.0007	124.87	12.487	5	2.5
trans-2-Butene	.0217	153.93	15.383	20	10
cis-2-Butene	.0190	180.91	18.091	5	2.5
n-Pentane	.0009	203.05	20.305	5	2.5
1,3-Butadiene	.0030	221.10	22.110	5	2.5

Experimental Procedure

A typical experimental run is listed in Table II. It demonstrates the profile with respect to pressure and temperature. These curves are illustrated in Figure 6. For this particular run, a sample of gas weighing 7.55 grams was charged into an evacuated sample bomb. The sample was transferred to the evacuated reactor with a 22 gauge syringe needle. After two minutes, a 0.1 ml sample of gas was taken with a 0.1 ml Hamilton gas-tight syringe from the septumized outlet valve and injected into the GC-4 chromatograph.

TABLE II

EXPERIMENTAL DATA FOR RUN 615-6U

Sample Weight, gms	7.44
Atmospheric Pressure, mm H_g	588.5
Atmospheric Temperature, °C	24.0

Time, (sec)	Press., (psig)	Thermo-couple Temp.(°C)	Heater Volt., (Volts)	Heater Amperes, (amp)	Gen. Amperes, (amp)	Gen. Freq. kHz
0	17	24	10.7	4.4	.1	26.5
30	26	42	10.7	4.4	.1	26.5
60	31	69	10.7	4.4	.1	26.5
90	35	95	10.7	4.4	.1	26.5

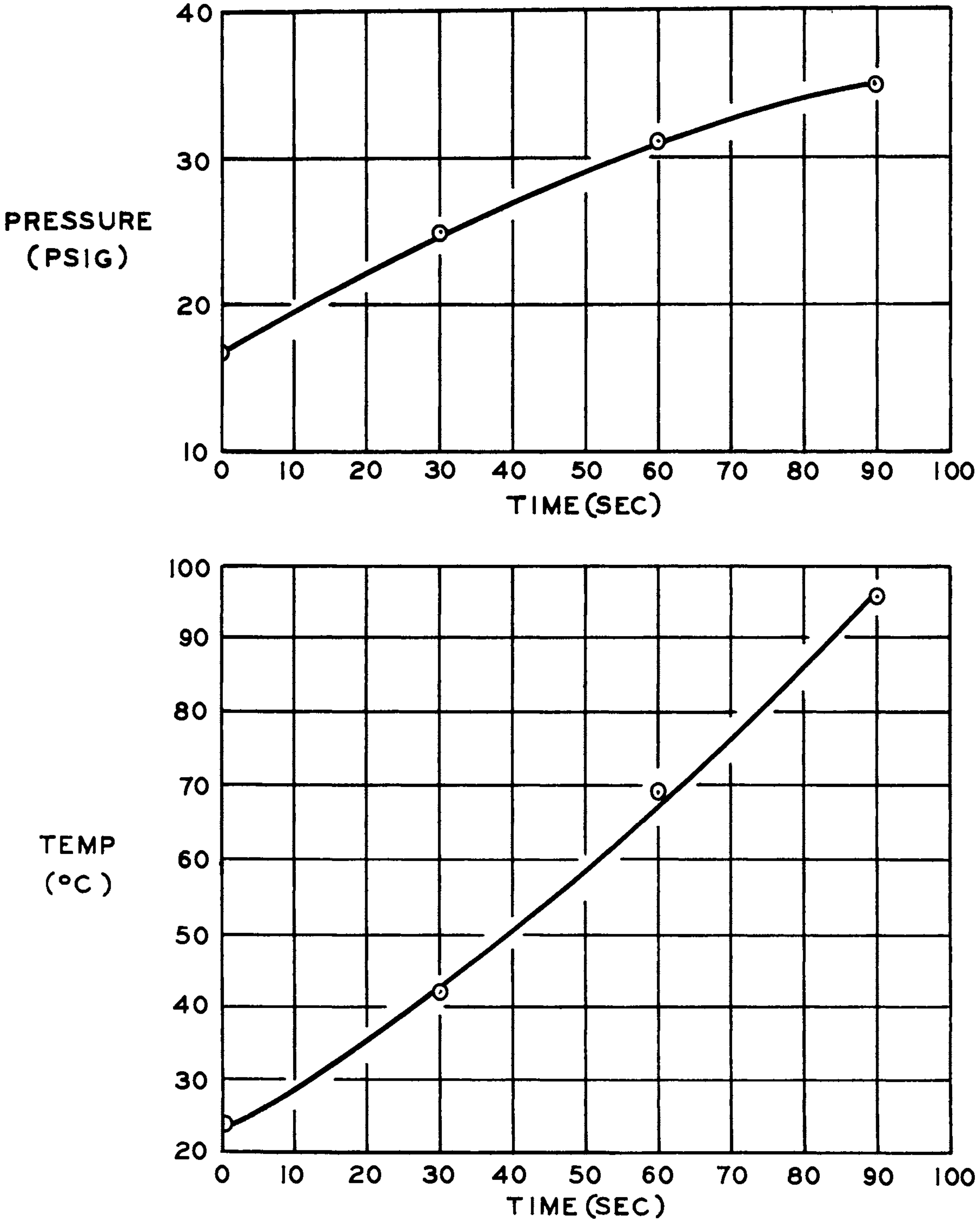

FIGURE 6 TEMPERATURE AND PRESSURE PROFILE WITH RESPECT TO TIME FOR RUN NO. 615-6U

CHAPTER IV

DISCUSSION

One hundred and fifty experimental runs were made. These runs were separated into three groups, fifty experimental runs per group. The raw data are located in the Appendices A, B and C.

Statistical Evaluation of the Results

Table III lists the mean data for each component in the gas mixture, their standard deviations, and the t-ratios.

The statistical t-ratio test was performed in order to determine the significance between the treatment Groups A, B and C. First, note that there is a difference in the concentrations of n-butane with a corresponding change in concentrations of the other components in the mixture between the treatment groups. Group C has the lowest concentration of n-butane. Second, the t-ratio test demonstrates that there is statistical significance for all of the components between Groups A and B except *trans*-2-butene. The same holds true for the relationship between Groups A and C. Ethane concentration probably would have been significant between these groups if the concentration of ethylene was separated from the concentration of ethane. However, ethane and ethylene could not be separated chromatographically. If an estimating procedure was undertaken to distinguish ethylene from ethane and the results tabulated accordingly, a certain amount of

TABLE III

ANALYTICAL DATA AND T-RATIOS

Variable	Group A		Group B		Group C			t-Ratios	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	A - B	A - C	B - C
Methane	.0003	.00056	.00114	.0010	.0030	.0090	5.1656***	2.0596*	1.3742
Ethane	.0001	.00034	.00133	.0008	.0061	.0249	9.5210***	1.6469	1.3097
Propylene	.0102	.02174	.09413	.0304	.1265	.0444	15.3976***	16.1162***	4.1203***
Propane	.0024	.00666	.03003	.0092	.0400	.0153	16.6483***	15.4514***	3.8369***
iso-Butane	.3585	.07566	.68053	.0760	.7711	.0831	20.5893***	25.1815***	5.5168***
n-Butane	99.5915	.09964	99.15732	.1062	99.0168	.1424	20.4388***	22.6679***	5.4227***
1-Butene	.0007	.00062	.00188	.0009	.0023	.0009	7.4021***	9.7748***	2.0890*
trans-2-Butene	.0217	.00327	.02257	.0048	.0233	.0011	1.0860	3.2280**	.9758
cis-2-Butene	.0190	.00267	.00943	.0005	.0094	.0011	3.7049***	3.4996***	.0551
n-Pentane	.0009	.00040	.00015	.0001	.0001	.0001	12.1481***	12.4765***	.8079
1,3-Butadiene	.0030	.00070	.00151	.0003	.0014	.0003	13.8218***	14.8494***	1.6438

* >P(0.05)   ** >P(0.01)   *** >P(0.001)

precision would be sacrificed especially since an estimate of this value would be extremely difficult to obtain. Empirically, however, approximately 50% of the ethane tabulated for Group C is, in fact, ethylene. This is not the case for Group B. At no time was there any indication that ethylene was present in Group B.

The t-ratio test between Groups B and C show significance for propylene, propane, i-butane, n-butane, and 1-butene. Ethane and ethylene would also have been significant for the reason suggested previously.

Table IV lists the reaction parameters. Reaction time, reaction temperature and the change in pressure show statistical significance. Since the sample weight was held constant between Groups B and C, it is evident that this parameter would not be significant.

In order to further test the effect of ultrasonic energy and determine an interaction between the parameters listed, an analysis of covariance was undertaken. The analysis of covariance was done on a Burroughs B5500 computer. Table V partially represents the results if the concentration of n-butane is held constant along with making one or more of the parameters covariates. Atmospheric pressure and temperature were always considered as covariates, since these parameters hardly varied throughout the experiment. As long as the concentration of n-butane is held constant, regardless of what other parameters are also held constant, the accompanying statistical F-test is not significant (Table V). However, if the concentration of n-butane is not held constant then, as is seen in Table VI, statistical significance is evident in all cases. The greatest statistical significance for the components, propane, propylene, i-butane and n-butane is demonstrated when change

TABLE IV

REACTION PARAMETERS AND t-RATIO

Parameter	Group B		Group C		t-Ratio
	Mean	Std. Dev.	Mean	Std. Dev.	
Reaction Temperature, °C	48.596	19.221	63.255	29.019	2.887*
Reaction Time, min	4.404	1.973	3.396	1.575	2.738*
Sample Weight, gm	16.517	8.518	14.306	7.892	1.306
Change in Pressure, psig	26.277	16.162	36.426	18.975	2.792*

* >P(0.05)

TABLE V

ANALYSIS OF COVARIANCE (F-TEST VALUES)
(n-BUTANE HELD CONSTANT)

Covariates Dependent Variables	1,2	1,2,3	1,2,4	1,2,5	1,2,6	1,2, 3,4	1,2, 3,5	1,2, 3,6	1,2, 4,5	1,2, 4,6	1,2, 5,6	1,2, 3,4,5	1,2, 3,4,6	1,2, 4,5,6	1,2, 3,5,6	1,2,3, 4,5,6
df	89	88	88	88	88	87	87	87	87	87	87	86	86	86	86	85
Methane	1.051	.726	.468	1.081	.722	.388	.507	.254	.327	.184	.723	.148	.063	.193	.264	.056
Ethane	0.411	.227	.263	.450	.384	.193	.134	.102	.258	.220	.382	.193	.077	.225	.095	.065
Propylene	.389	.741	.035	1.047	.124	.125	2.846	.528	.313	.039	.149	.125	.030	.001	1.092	.345
Propane	1.207	.730	.183	2.843	1.702	.127	2.001	.797	.887	.277	1.838	.127	.127	.492	1.154	.334
i-Butane	.025	.098	.052	.300	.032	.013	1.048	.214	.025	.078	.039	.013	.000	.016	.452	.084
1-Butene	.045	.206	.884	.000	.421	1.003	.140	.137	.845	.014	.410	1.00	.036	.085	.070	.209
t-2-Butene	.320	.024	.286	.857	.791	.114	.069	.039	1.049	.784	.807	.114	.156	.987	.050	.218
c-2-Butene	.156	1.051	.472	.019	.001	1.032	.615	.929	.004	.073	.003	1.03	.914	.016	.803	.710
n-Pentane	.341	.045	.148	1.262	1.499	.045	.359	.432	1.089	1.089	1.529	.045	.447	1.324	.499	.527
1,3-Butadiene	.159	.754	.462	.001	.109	.830	.455	.119	.042	.004	.0111	.830	.147	.007	.134	.181

1 = Atmospheric temperature
2 = Atmospheric pressure
3 = Time
4 - Sample size
5 = Change in pressure
6 - Reaction temperature

>P(0.05) = 3.95
>P(0.01) = 6.93
>P(0.001) = 10.90

TABLE VI

ANALYSIS OF COVARIANCE (F-TEST VALUES)
(n-BUTANE NOT HELD CONSTANT)

Covariates Dependent Variables	1,2	1,2,3	1,2,4	1,2,5	1,2,6	1,2, 3,4	1,2, 3,5	1,2, 3,6	1,2, 4,5	1,2, 4,6	1,2, 5,6	1,2, 3,4,5	1,2, 3,4,6	1,2, 4,5,6	1,2, 3,5,6	1,2,3, 4,5,6
df	90	89	89	89	89	88	88	88	88	88	87	87	87	87	87	86
Methane	3.76	3.13	3.71	2.53	3.09	3.09	1.27	2.04	2.09	3.01	2.52	1.10	2.02	2.12	1.23	1.09
Ethane	2.89	2.38	2.89	1.74	2.81	2.28	.75	1.94	1.89	2.88	1.95	.90	1.88	2.02	.90	.99
Propane	15.85***	16.80***	22.66***	4.14*	15.29***	21.33***	3.01	17.04***	10.29**	24.48***	7.77**	7.44**	22.55***	14.04***	6.50*	11.00***
Propylene	14.37***	13.40***	19.11***	3.88	15.80***	16.65***	1.38	14.32***	8.70**	23.53***	8.18**	4.25*	18.60***	13.09***	4.27*	7.50**
i-Butane	23.40***	23.79***	28.88***	10.53**	23.74***	27.20***	27.20***	24.92***	17.16***	31.75***	15.45***	13.65***	29.32***	21.22***	13.34***	17.67***
n-Butane	25.05***	24.92***	33.27***	10.37**	25.38***	30.77***	7.40**	25.62***	18.64***	39.96***	16.66***	13.63***	32.70***	24.45***	13.03***	18.85***
1-Butene	1.69	1.18	1.67	1.02	4.68*	1.20	.20	3.63	.58	4.53*	2.34	.08	3.63	1.36	.99	.58
t-2-Butene	.98	.36	.97	1.84	1.70	.32	.28	.42	2.29	1.72	1.99	.53	.38	2.34	.32	.52
c-2-Butene	.29	1.36	.30	.11	.01	1.34	.59	1.20	.07	.02	.10	.54	1.18	.07	.67	.61
n-Pentane	1.86	3.09	2.01	.01	.67	2.94	.11	1.89	.02	.89	.00	.26	1.82	.04	.22	.34
1,3-Butadiene	3.54	5.71*	3.77	.47	1.46	5.53*	1.90	3.60	.98	1.78	.44	2.47	3.52	.88	1.88	2.33

1 = Atmospheric temperature
2 = Atmospheric pressure
3 = Time
4 = Sample size
5 = Change in pressure
6 = Reaction temperature

* >P(0.05) = 3.95
** >P(0.01) = 6.93
*** >P(0.001) = 10.90

in reaction chamber pressure is allowed to vary. The most prominent parameter is the change in pressure. Reaction time seems to be the next most effective parameter. If time is omitted as a covariate, i.e., time is allowed to vary, more significance can be attached to the concentrations of the individual components in the gas mixture. The data indicates that there is a significant difference between Groups B and C.

If ultrasonic energy did not affect the pyrolysis of n-butane, there would be no difference between Tables V and VI. The comparison of these Tables very clearly indicate that significantly more n-butane is pyrolyzed when n-butane is irradiated with ultrasonic energy. Therefore, ultrasonic energy does affect the pyrolysis of n-butane.

Table VII is a tabulation of a linear stepwise regression analysis which was used to further verify the above results and to determine if it was possible to predict the concentrations of the particular components from the parameters recorded during an experimental run. Table VII is composed of the respective coefficients and constants for each multiple regression analysis.

The equation used is of the form:

$$Y = A_1 X_1 + A_2 X_2 + A_3 X_3 + \ldots B \qquad (16)$$

where Y = predicted concentration of quantities listed in dependent variable column

A = coefficient to be multiplied by respective raw data

B = numerical constant for the regression equation

$X_{1,2,3}$ = independent variables

The coefficients predicting the concentration of each component are different for each group. The multiple correlation coefficient (Mult. R) is significantly different from zero indicating an excellent

TABLE VII

STEPWISE REGRESSION COEFFICIENTS

Treatment	Dependent Variable	Atmospheric Pressure (mm Hg)	Time (min)	Sample Size (gms)	Change in Pressure (psig)	Reaction Temp. (°C)	Constant	Mult. R	Std. Error
Heat	Ethane	-0.00011	0.00012	0.0001	-0.0030		0.067	0.42**	0.008
			0.00019	0.00005	0.00006	-0.00009	0.00244	0.38**	0.0008
Sound	Ethane	-0.0003	-0.0003	0.0005	0.00012		1.784	0.33*	0.02
			-0.0003	0.00035	0.00020		0.00413	0.22	0.0251
Heat	Propane	0.00122		0.00375	0.00103	-0.00193	-0.61608	0.53***	0.03
			-0.00105	0.00340	0.00042	-0.00126	0.09281	0.53***	0.0268
Sound	Propane		0.00051	0.00213	0.00130	-0.00045	0.0756	0.76***	0.03
Heat	Propylene		-0.00084	0.00119	0.00022	-0.00051	0.03319	0.61***	0.0076
Sound	Propylene		-0.00187	0.00068	0.00052	-0.00017	0.02875	0.77***	0.01
Heat	i-Butane	0.00514	-0.00739	0.00565	0.00204		-2.347	0.46**	0.07
			0.00939	0.00474	-0.00366	0.00166	0.658	0.44**	0.07
Sound	i-Butane		0.00952	0.00341	0.00210	-0.00092	0.672	0.74***	0.058
Heat	n-Butane		0.01099	-0.01070		0.00324	99.128	0.51***	0.09
Sound	n-Butane	0.00613	-0.00432	-0.00713	0.00398	0.00146	95.579	0.78***	0.09
			-0.00386	-0.00669	-0.00420	0.00154	99.181	0.78***	0.09

* >P(0.05) = .288 ** >P(0.01) = .372 *** >P(0.001) = .465

correlation with the experimental data. These factors lead to the conclusion that Group C is significantly different from Group B.

In order to substantiate the reproducibility of the results, a linear stepwise regression for the prediction of n-butane was computed for each treatment group. Table VIII is a tabulation of these results. Coefficients listed in Table VIII are of the same form as in Table VII. The Multiple R in these cases further substantiate the claim that not only is tabulated data reproducible but also that ultrasonic energy affects the pyrolysis of n-butane.

Chemical Interpretation of the Results

Since the thermal decomposition of n-butane occurs entirely in the gas phase, the principle of cavitation cannot apply since cavitation can only occur in the liquid phase. The major reactions are of the Rice-type free radical mechanism pertaining to the major component, n-butane. However, since there were eleven components in the gas mixture, it is unreasonable to assume that these constituents do not also enter into the reaction. There necessarily must be an interaction between all of the components in the mixture.

Rice as well as Purnell and Quinn have shown that if the paraffin decomposes at a given cracking or thermal decomposition temperature then the corresponding olefins will decompose at a temperature less than or equal to the same temperature of the paraffin. The olefin is usually considered more subject to thermal decomposition than its corresponding paraffin due to its structure.

TABLE VIII

STEPWISE REGRESSION FOR PREDICTION OF n-BUTANE CONCENTRATION

Predicted Component	Propane	Propylene	i-Butane	t-Butene	Constant	Mult. R	Std. Error	Efficiency of Prediction
S-n Butane	- .69	-2.02	-1.02		99.97	.975***	0.0326	95.1%
H-n Butane	- .997	-1.003	- .999	- .930	100.01	.999***	.0019	99.7%
C-n Butane	-1.129	-0.653	-1.003	-1.004	100.00	1.000***	.9996	100%

*** >P(0.001)

In Groups B and C, n-butane is the principal material that decomposes. The decomposition of n-butane most probably follows those reactions listed from No. 1 to No. 8 in Chapter II. However, from Table III, the concentration of 1-butene significantly increases. There is a small increase in the concentration of <u>trans</u>-2-butene, but a decrease in the concentration of <u>cis</u>-2-butene and 1,3-butadiene. For n-pentane, there is an increase in concentration in Group B, but a decrease in concentration in Group C. A probable explanation of these findings is that the key free radicals, methyl ($CH_3\cdot$) and ethyl ($C_2H_5\cdot$) recombine with various components to form the indicated products. Whitten and Rabinovitch (39) postulated the formation of isobutane from propane and methyl radical. In addition to the reactions already given, there is evidence that the following reaction mechanisms can occur:

$$C_3H_6 + 2H\cdot \quad \rightleftarrows \quad C_3H_8 \qquad (17)$$

$$C_4H_6 + 2H\cdot \quad \rightleftarrows \quad C_4H_8 \qquad (18)$$

$$C_3H_5 + CH_3\cdot \quad \rightleftarrows \quad i\text{-}C_4H_{10} \qquad (19)$$

A material balance over 1,3 butadiene and 1-butene fairly well substantiates Equation 18. The material balance was calculated from the data in Table II by comparing the mole percent difference of 1-butene and the mole percent difference of 1, 3-butadiene between Groups A and C. For 1-butene there is an increase of 0.0016 mole percent and a decrease of 0.0016 mole percent for 1,3-butadiene, the net difference is therefore zero. If one compares the difference between the material balance of Group C with Group A, the net difference is +0.0040 whereas the net difference between Group B and Group A is -0.0083.

Using the stepwise regression analysis noted in Table VIII, a material balance can be applied as a check to determine the veracity of the claim that with ultrasonic energy, the kinetics of the decomposition of butane is different than the decomposition of butane with heat energy alone. With sound energy, n-butane primarily decomposes to propane, propylene and i-butane, while with heat energy alone, n-butane decomposes to propane, propylene, i-butane and t-2-butene. With respect to the material balance, the net difference between Groups C and A is -0.0082 whereas the net difference between B and A is +0.00028. As the stepwise regression indicates, these net differences are well within experimental error.

Unfortunately, a hydrogen balance could not be determined analytically to substantiate the above premises. Obviously hydrogen was produced, but because of the low conversion rate of n-butane, the concentration of hydrogen produced was too low to be detected by a chromatographic instrument using a thermal conductivity detector. The more sensitive hydrogen flame ionization detector cannot detect hydrogen.

The additional mechanisms presented here (Equations 12 - 19) may be the result of the particular system used. Since there is evidence that indicates this reaction is surface sensitive, the surface of the transducer may have catalyzed the decomposition reaction.

Another possible explanation is that this reaction was activated in a helium atmosphere. According to El'piner (7), helium "can intensify ionization processes." Therefore, a synergism may exist between the helium and the ultrasonic energy to produce favorable results. As a matter of fact, this principle has been used to considerable advantage in the production of a Helium Detector for a Gas

Chromatographic system (13).

Physical Interpretation of the Results

The statistical significance of Group C over Group B is chiefly due to the action of ultrasonic energy on the gas molecules as they collided with the hot nichrome wire, and then interacted with each other. The molecular acceleration forces that are present when ultrasonic energy is applied to a fluid system can be shown by considering the basic equations for amplitude, pressure, velocity and acceleration in the case of a plane progressive wave acoustic field. The acoustic energy density (ergs/cm^3) contained in a unit of volume of the fluid is:

$$W = \frac{I}{c} \qquad (20)$$

where W = acoustic energy density, ergs/cm^3.

I = amount of energy which is propagated each second through the unit of surface area, ergs/cm^2.

c = speed of sound through the medium of propagation, cm/sec.

Acoustic intensity is related to the vibratory amplitude by

$$I = 1/2\ dcA^2w^2 \qquad (21)$$

where **d** = density of the fluid at a mean temperature, gm/cm^3.

A = maximum elongation along the propagation axis, cm.

w = angular frequency or $2\pi f$.

f = vibration frequency of the sound energy, kHz.

Intensity, I, is also given by:

$$I = 1/2\ p^2/dc \qquad (22)$$

where p = acoustic pressure amplitude, dynes/cm^2.

Therefore,

$$p = \sqrt{2dcI} \qquad (23)$$

The velocity amplitude, V (cm/sec), is also related to the intensity by:

$$V = \sqrt{2I/dc} \qquad (24)$$

The acceleration amplitude, a, cm/sec^2, is:

$$a = wV = w\sqrt{\frac{2I}{dc}} = 2\pi f \sqrt{\frac{2I}{dc}} \qquad (25)$$

When the above equations are solved for the conditions used in this study, the value of the molecular acceleration is 6900 G's or 6900 times greater than the acceleration due to the force of gravity. In simple terms, when ultrasonic energy is applied to a fluid system, the molecules within that system are accelerated with a force equal to 6900 G's. In this experiment, the activation energy for reaction was assumed to be imparted to the molecules by the introduction of heat energy from the heating coil. For a first approximation, the acceleration forces are assumed to merely increase the frequency of the collision of the molecules with the heating coil thereby producing the decomposition of n-butane. The conversion was not very large because the surface area of the heating coil was not very great. The ultrasonic energy, therefore, acted as a very efficient stirrer. The considerable oscillation of the pressure gauge in the system (approximately 40 - 50 units) gave evidence to this fact. This oscillation was not present when just heat energy was applied (Group B).

There is some evidence that ultrasonic energy could accelerate chemical reactions (21). However, the chief mechanism that caused the statistical significance between Groups B and C seems to be the acceleration of the molecules colliding either on or off the hot surface. The molecules colliding with the hot surface would be replaced by other molecules that would undergo the very same procedure.

The fact that ultrasonic energy in interaction with the barium titanate transducer may have caused a peculiar reaction was indicated on three separate occasions. The same results occurred in all three instances. When the transducer had aged (carbonized) to a certain point, for some unexplainable reason, aromatics were produced and about 14% of the n-butane was decomposed. Instead of analytically separating eleven components as was usually the case, some twenty components were analytically separated. From infrared analysis, aromatics were detected but their structure could not be exactly determined.

That a violent reaction had occurred was obvious, upon opening the reaction chamber. There was a considerable amount of carbon deposited throughout the chamber, and the heating coil was out of position. On one of these occasions, the stainless steel thermocouple sheath was bent at an angle of 20°.

After these episodes, the chamber was cleaned with acetone, ether, and ethanol thoroughly. The chamber was then closed, sealed and purged with helium for approximately two hours. The experimental runs made after this procedure were the same as before.

On these three occasions several runs were made prior to cleaning and these were alternately heat runs and ultrasonic runs. A heat run did not show evidence of any products but the eleven usually analyzed.

From Table VII, the concentration of n-butane can be determined by correlating the physical parameters in a linear fashion. The concentration of n-butane when only heat energy is applied is predicted by the following equation:

$$\text{n-butane (wt. \%)} = .01099\,(t) - 0.0107\,(S) + .00324\,(T) + 99.128 \qquad (23)$$

where

t = time, min

S = sample size, gms

T = temperature, °C

The concentration of n-butane when sonic energy is applied can be predicted by

$$\text{n-butane} = .00386\,(t) - 0.00669\,(S) - 0.00420\,(\ \ P) + 0.00154\,(T) + 99.187 \qquad (24)$$

where P = change in pressure, psig

If equation 23 is used to predict the concentration of n-butane using the mean values listed in Table IV the following is the result:

	n-Butane (Heat)	n-Butane (Sound)
Equation 23	99.157	99.217
Equation 24	99.018	99.016

From the data, it is obvious, that in both cases more n-butane will be decomposed using sonic energy than using heat energy. The exact relationship of temperature to the kinetics of the decomposition of n-butane is masked due to the interaction of the other feed components within the system. Other investigators have published kinetic data based on a pure sample of n-butane where, in fact, they did not have a pure sample. The purity of their feed may explain why various investigators have published what seems to be conflicting results with respect to the frequency factor and the activation energies.

CHAPTER V

SUMMARY

An experiment was run in a batch system to determine the affect of ultrasonic energy on the pyrolysis of n-butane. This experiment was statistically designed to include three treatment groups, a control group, a heat group, and an ultrasonic group. An equal number of experimental runs was made in each group in order to facilitate statistical analysis.

No treatment was applied to the control group, heat energy was applied to the heat group, and ultrasonic and heat energy was simultaneously applied to the ultrasonic group. The temperature at which the reaction occurred was nominally set at 400°C, the initial pressure at 15 psig and the frequency of the ultrasonic energy at 28.3 kHz. The operating parameters such as reaction time, final reaction temperature, initial weight of the sample and the change in pressure were allowed to vary and statistically analyzed.

The data indicated that ultrasonic energy did affect the thermal decomposition of n-butane. Ultrasonic energy accelerated the reaction such that a greater percentage of n-butane was decomposed with ultrasonic energy than without ultrasonic energy. The experimental data were substantiated statistically at the 99.9% confidence level. The concentrations of propane, propylene, i-butane, and n-butane were most affected by the additional treatment. All this occurred in 25% less time than with just heat energy. The product distribution differed from the product distribution reported by Purnell and Quinn.

A Rice-type free radical mechanism is postulated to explain these findings. A theoretical postulate is also presented to explain why ultrasonic energy can influence the reaction.

CHAPTER VI

CONCLUSIONS

Since the experimental results proved to be reproducible, ultrasonic energy did influence the thermal decomposition of n-butane. Statistically, this effect has a confidence level of greater than 99.9% Upon the addition of ultrasonic energy, more n-butane was decomposed in 25% less time on the average. This effect had a statistical confidence level of greater than 95%. When n-butane decomposed, the major products were lower boiling than butane. This effect had a statistical confidence level of greater than 99.9%. Since the n-butane used contained other components, these other components interacted and were also affected by ultrasonic energy. Of the ten other components, the chief components that were affected were propane, propylene, and i-butane. Statistically the confidence level of this effect was greater than 99.9%.

During this series of experiments a statistical regression model was derived that conclusively demonstrates the benefit of employing ultrasonic energy in conjunction with heat energy to thermally decompose n-butane. No credit was given in this model for the effect of the surface of the ultrasonic transducer. The surface of the transducer may have had catalytic properties.

CHAPTER VII

RECOMMENDATIONS

Now that a statistical model has been established, further investigation on the overall process can be initiated. The effect of higher ultrasonic frequencies and intensities, and the effect of higher temperatures on conversion and selectivity to particular product distributions must be studied.

Future investigators should try to ascertain the effect of ultrasonic energy on the initial reaction rates. In order to examine the initial reaction rates, ultrapure n-butane and a continuous flow system are recommended. The continuous flow system is a necessity in order that secondary competing reactions are quenched as rapidly as possible. Therefore, the reaction chamber should be relatively small (ca 1 - 2 cc), the residence time short (ca 1 - 2 milliseconds). The above conditions should tend to reduce the possibility of secondary reactions from occurring. Analytical equipment to analyze the product distribution should be in-line with the reaction chamber and should consist of a gas-liquid chromatographic instrument that has as its detector, a real time mass spectrograph.

BIBLIOGRAPHY

(1) Balakishiev, G. A., Ismailov, R. G., Korneev, M. I., and Mezhchovskii, E. B. "Effect of Ultrasonic Energy on Cracking of a Solar Oil Distillate." Izv. Vsysshikh Uchebn. Zavedenii Neft i Gaz. 5. (1962), 59.

(2) Balakishiev, G. A., Ismailov, R. G., Korneev, M. I., and Mezhchovskii, E. B. "Effects of Ultrasonic Energy on the Quality of Cracking Gasoline and Gas in the Cracking of Solar Oil Distillates." Izv. Vsysshikh Uchebn. Zavedenii Neft i Gaz. 8. (1965), 71.

(3) Bobkiewicz, H. "Application of Ultrasonics in (Industrial) Practice." Chemik. 18. (1965), 126.

(4) Brodskii, A. M., Zoonor, N. V., Lavrovskii, K. P., and Titov, V. B. "Thermal and Radiation Conversions of Petroleum Fractions." Neftekhimiya. 1. (1961), 370.

(5) Coffin, C. C., and Funt, B. L. "The Effect of Sound Waves on Fractional Distillation." J. Phys. Chem. 53. (1949), 891.

(6) Einstein, A. "The Velocity of Sound in Partially Dissociated Gas." Sitz. Preuss. Akad. Wiss. Berlin Math Naturw. Kl. (1920), 380.

(7) El'piner, I. E. Ultrasound, Physical, Chemical, and Biological Effects. New York: Consultants Bureau. (1964).

(8) Fogler, H. S. "Applications and Research in Sonochemical Engineering." Sound and Vibration. 1. (1967), 1.

(9) Fogler, H. S. "The Influence of Reacting Gases on the Motion of Collapsing Cavities." Chem. Eng. Science 24. (1969), 1043.

(10) Frederick, J. R. Ultrasonic Engineering. New York: John Wiley and Sons, Inc. (1965).

(11) Greguess, P. "Ultrasonic Vibrations and Their Use in the Chemical Industry." Przem. Chem. 4. (1956), 226.

(12) Haissinsky, M., and Prudhomme, R. P. "Remorques sur le Micanisme des Actions Chimiques Prodiutes por les Ultrasons." J. Chem. Physique et Physico. Chim. Biol. 47. (1950), 925.

(13) Hartmann, C. H., and Thompson, K. "Helium Detector for PPB Analysis of Fixed Gases." Aerograp Res. Notes, (Aerograph Brochure). (1967), 8.

(14) Ilibontry, L. "The Effect of Ultrasound Waves on Some Chemical Reactions." J. Chim. Phys. 41. (1944), 173.

(15) Lindstrom, O. "Reaction Sites in a Field of Stationary Ultrasonic Energy." J. Chem. Phys. 19. (1951), 1613.

(16) Lynnworth, L. I. "Ultrasonic Impedance Matching From Solids to Gases." Presented at the 68th meeting of the Acoustical Society of America, October 22, 1964.

(17) Nosov, V. A. Ultrasonics in the Chemical Industry. New York: Consultants Bureau. 2. (1965).

(18) Ockubloom, N. E., and Stuart, A. P. "Propylene Shortage Coming?" Hydro. Proc. 46. No.5. (1967), 225.

(19) _____, "Midyear Report", Oil and Gas J., 68. No.30. (1970), 98.

(20) Parthasarathy, S., Pancholy, M., and Saksena, T. K. "Effect of Ultrasonic Waves on the Esterification of Ethanol." Curr. Sci. 31. (1958), 500.

(21) Pribnow, V., and Alexandrescu, M. "The Chemical Effects of Ultrasonics." Rev. Chim. (Bucharest). 11. (1960), 293.

(22) Prudhomme, R. O., and Grabar, P. "Etude de la Denaturation des Proteides. I. Action des Ultrasons sur les Proteides du Serum de Cheval Normal et sur les Acides Amines Cycliques." Bull. Soc. Chim. Biol. 29. (1947), 122.

(23) Purnell, J. H., and Quinn, C. P. "The Pyrolysis of n-Butane." Roy. Proc. Soc. A270. (1962) 18.

(24) Rice, F. O. The Mechanism of Chemical Homogenous Organic Reactions from the Physical Standpoint. New York: Chemical Catalog Co. (1931).

(25) Rozycka, D. "Ultrasonics in the Chemical Industry." Chemick. 18. (1965), 91.

(26) Sagert, N. H., and Laidler, K. J. "Kinetics and Mechanisms of the Pyrolysis of n-Butane." Can. J. of Chem. 41. (1963), 838.

(27) Sandler, S., and Lanewala, M. A. "Pyrolysis of n-Butane in a Differential Flow Reactor." J. of Chem. Eng. Data 8. No. 2 (1963), 258.

(28) Schenck, G. O., Foldiak, G., and Meder, W. "Boundary Temperature in the Irradiated Chemical Thermal Cracking of Paraffins." Naturwissenschaften. 48. (1961), 571.

(29) Schmid, G. "Zerreissen von Makromolekulen Versuch liner Erklarung of Depolymerisierenden Wirkung von Ultraschallwellen." Phys. Z. 41. (1940), 325.

(30) Siegel, G., Pfennigsdorf, G., and Monig, H. "Untersuchungen uber die Reduktionsbeschleunigende Wirkung des Ultraschalls." Naturwissenechaften. 45. (1958), 415.

(31) Steacie, E. W. R. Atomic and Free Radical REactions. New York: Reinhold Publishing Co. Vol. I and II, 2nd Ed. (1954).

(32) Stobaugh, R. B. "Ethylene: How, Where, Who-Future." Hydro. Process. 45. No. 10. (1966), 143.

(33) Szent-Gyorgyi, A. "The Chemical and Biological Effects of Ultrasonic Radiation." Nature. 131. (1933), 278.

(34) Torok, J. and Sandler, S., "Kinetics of the Pyrolysis of n-Butane." Can. J. Chem. Eng. 47. (1969), 3863.

(35) Wang, Y-L., Rinker, R. G., and Corcoran, W. H. "Kinetics and Mechanism of the Thermal Decomposition of n-Butane." I&EC Fund. 2. No. 3. (1963), 161.

(36) Weiss, A. H., "Propylene: How to Meet Future Needs." Hydro. Proces. (October, 1969), 125.

(37) Weissler, A., Cooper, H. W., and Snyder, S. "The Chemical Effects of Ultrasonic Irradiation Reaction Between CCl_4 and H_2O." J. Acoust. Soc. Am. 20. (1948), 89.

(38) Winger, J. G., "The Petroleum Situation", A Monthly Review from the Energy Division of the Chase Manhattan Bank, New York, (November 30, 1970).

(39) Whitten, G. Z. and Rabinovitch, B. S., "The Chemically Activated Decomposition of n-Butane and of Isobutane." J. Phys. Chem. 69, No. 12. (1965), 4348.

(40) Zdonik, S. B., Green, E. J., and Hallec, J. P., "Expansion Programs (for Ethylene and Derivatives) are geared to 7% annual Additional Capacity." Oil and Gas J. 64. No. 49. (1966), 108.

APPENDIX A

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP A)

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP A)

Chromatographic Data (Peak Areas, cm^2)

Identification Number	Methane	Ethane	Propylene	Propane	Isobutane	n-Butane	1-Butene	t-2-Butene	c-2-Butene	n-Pentane	1,3-Butadiene
409-1	0.20	0.38	27.15	8.25	126.0	17600	0.16	3.80	1.53	0.08	0.25
409-4U	0.00	0.00	1.24	0.17	72.0	18900	0.00	4.05	1.86	0.12	0.69
409-2U	0.00	0.00	0.32	0.04	54.0	19300	0.00	4.10	1.93	0.23	0.53
409-3U	0.00	0.00	1.09	0.16	68.5	20250	0.00	4.15	1.94	0.18	0.53
409-5U	0.00	0.00	1.47	0.32	76.5	20400	0.00	4.40	2.01	0.17	0.54
411-1	0.00	0.00	1.16	0.11	62.0	18950	0.00	3.48	1.75	0.19	0.43
411-2	0.00	0.05	0.53	0.09	56.0	18450	0.00	3.75	2.64	0.16	0.65
411-3	0.00	0.00	1.51	0.25	72.0	18300	0.00	3.83	1.81	0.13	0.52
411-4	0.02	0.00	0.69	0.15	54.0	18100	0.00	3.75	1.86	0.13	0.55
411-5	0.00	0.00	0.85	0.16	71.0	20300	0.00	4.00	1.83	0.15	0.57
411-6	0.00	0.00	0.28	0.10	43.0	19400	0.00	4.28	2.05	0.37	0.83
504-2	0.00	0.00	8.56	1.92	402.5	101400	0.41	20.87	10.14	0.00	2.44
518-1	0.00	0.98	17.28	3.19	994.5	261600	1.64	61.63	25.66	1.81	6.94
520-1	0.00	1.17	21.30	4.24	1017.5	299800	0.00	65.40	25.95	2.53	8.68
519-1	0.00	0.93	19.53	4.04	946.0	230600	2.77	57.65	26.25	1.80	6.10
522-2	0.00	0.66	16.90	3.26	941.5	296280	0.00	62.63	25.23	2.01	8.44
502-1U	5.55	0.16	10.75	1.85	550.0	150100	0.84	33.73	14.91	0.90	8.56
503-2U	0.00	0.00	9.85	1.75	487.5	147000	0.89	29.61	13.86	0.85	4.28
503-3U	0.00	0.08	4.95	0.84	438.0	144600	0.64	29.76	12.75	1.46	4.24
503-1U	0.00	0.00	8.66	1.62	474.0	144000	0.93	29.28	13.33	1.09	4.44
503-4U	0.00	0.00	5.89	0.97	436.5	136600	0.83	27.64	13.95	1.00	4.16
523-2	0.77	0.04	25.45	5.07	1030.5	295100	0.99	64.13	26.95	1.77	7.79
524-2	0.34	0.00	5.96	0.84	744.0	293200	0.00	64.85	32.04	3.45	10.40
524-1	0.39	0.00	4.29	0.61	668.7	274500	0.69	58.55	29.76	3.76	10.33
525-1	0.72	0.02	14.05	2.79	902.0	280000	4.84	62.78	29.67	1.68	8.22
526-1U	0.58	0.03	16.13	2.60	904.5	273500	4.86	60.10	26.96	1.92	6.99
530-1U	0.18	0.07	25.38	6.19	502.5	112200	1.75	26.26	11.01	0.49	2.40
531-1	0.13	0.40	7.05	1.46	208.8	50550	0.71	5.94	5.46	0.34	1.36
529-1U	0.13	0.04	24.60	5.04	610.0	149600	2.14	33.24	15.06	0.76	3.15
601-1U	0.12	0.00	8.38	1.46	428.7	120275	1.52	28.96	13.55	1.63	3.59
602-1	0.55	0.18	96.05	27.90	2612.0	525100	3.68	130.78	59.46	3.24	16.44
613-1U	0.75	0.01	3.40	1.06	446.0	155900	0.00	39.98	19.32	2.74	6.33
614-1U	1.08	0.02	2.42	0.35	434.5	159700	0.36	38.46	17.45	3.18	7.03
615-1U	1.11	0.05	5.40	0.67	622.0	203300	1.45	47.62	23.86	2.75	7.19
617-1	0.64	0.02	8.37	1.23	652.5	193300	0.70	46.12	21.46	2.69	7.02
610-1	0.53	0.01	4.33	0.65	510.0	151050	0.00	39.46	17.37	2.90	6.34
618-1	0.43	0.03	8.28	1.72	289.0	70400	0.97	16.44	15.52	0.61	1.76
620-1	0.10	0.02	1.29	2.27	566.0	134700	1.87	33.17	16.32	1.24	4.43
623-1	0.37	0.02	15.30	3.04	510.0	125100	1.77	30.26	14.18	0.85	3.56
628-1U	0.19	0.00	9.28	1.65	430.0	109600	1.57	25.46	12.16	0.70	3.19
629-1U	0.28	0.00	10.14	1.70	373.0	96200	1.32	22.24	21.94	0.75	2.75
624-1	0.53	0.01	14.42	2.78	612.0	153800	2.16	36.34	17.20	1.23	4.63
621-1	0.08	0.02	13.00	2.42	540.0	140200	1.81	32.01	15.38	1.10	4.22
630-1	0.08	0.00	7.90	1.47	355.0	102000	1.28	21.40	10.61	1.05	3.27
701-1	0.45	0.02	16.62	3.32	411.1	121300	1.77	28.70	13.65	0.71	3.17
704-1	0.44	0.00	8.02	1.43	440.0	116900	1.52	27.10	12.40	1.03	3.23
705-1	0.10	0.00	12.18	2.74	497.0	118300	1.62	6.92	13.11	0.89	3.10

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP A)

Operating Conditions

Identification Number	Room Temperature (°C)	Atm. Press. (mm Hg)
409-1	25.0	590.0
409-4U	24.7	588.3
402-2U	24.7	588.7
409-3U	24.4	590.2
409-5U	24.8	591.0
411-1	25.0	590.3
411-2	25.1	588.4
411-3	24.0	590.2
411-4	23.9	589.3
411-5	23.8	589.2
411-6	24.1	592.0
504-2	27.0	592.5
518-1	25.0	587.5
520-1	24.0	585.7
519-1	24.0	588.3
522-2	24.5	581.4
502-1U	26.0	594.7
503-2U	27.0	592.3
503-3U	27.0	592.1
503-1U	26.0	592.8
503-4U	28.0	592.1
523-2	24.5	586.5
524-2	24.7	589.1
524-1	24.5	589.7
525-1	24.7	588.7
526-1U	24.0	587.4
530-1U	24.0	587.0
531-1	24.1	588.5
529-1U	24.0	587.5
601-1U	24.0	587.1
602-1	24.0	581.8
613-1U	23.9	592.6
614-1U	25.6	592.5
615-1U	24.6	588.5
617-1	23.9	588.5
610-1	24.1	586.0
618-1	23.9	588.2
620-1	24.0	587.3
623-1	23.6	584.7
628-1U	23.9	588.9
629-1U	23.9	587.5
624-1	24.0	583.5
621-1	23.9	586.8
630-1	23.2	587.3
701-1	23.2	587.0
704-1	23.9	588.2
705-1	23.6	587.8

APPENDIX B

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP B)

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP B)

Chromatographic Data (Peak Areas, cm^2)

Identification Number	Methane	Ethane	Propylene	Propane	Isobutane	n-Butane	1-Butene	t-2-Butene	c-2-Butene	n-Pentane	1,3-Butadiene
519-1	1.87	3.03	279.00	86.85	1791.00	232500	4.75	51.00	21.37	0.23	2.95
520-1	0.88	1.81	164.25	50.80	1245.00	186800	2.30	41.58	18.04	0.00	2.72
520-2	0.94	1.55	161.00	50.00	1295.00	211000	0.85	45.15	19.50	0.00	3.14
520-3	6.05	6.55	239.25	80.00	1648.00	236500	0.50	50.00	20.58	0.00	6.29
521-1	1.55	2.11	163.50	51.35	1352.00	224800	0.0	48.10	20.16	0.58	3.31
521-2	2.42	4.00	174.50	55.60	1268.00	187600	3.85	40.35	17.03	0.21	2.33
522-2	0.86	2.01	232.00	71.00	1594.00	237600	1.76	51.50	21.07	0.0	3.02
522-1	6.36	6.81	165.75	55.65	1222.00	187800	2.31	41.40	17.37	0.32	2.55
523-1	0.56	1.44	166.00	49.30	1316.00	207400	2.22	45.87	18.70	0.42	2.87
523-2	1.18	1.53	165.75	52.00	1287.00	204700	2.11	42.90	18.38	0.41	2.84
523-3	0.77	3.69	275.25	88.50	1664.00	228600	2.81	50.35	19.60	0.16	2.76
524-1	1.09	1.58	139.75	42.85	1215.00	199200	1.51	43.45	17.61	0.37	3.09
524-2	0.51	1.37	171.50	50.80	1333.50	204300	3.43	44.53	18.06	0.25	2.78
524-3 (A)	1.27	2.35	170.00	53.85	1213.50	179700	2.61	40.32	16.40	0.41	2.37
525-1	0.97	1.49	165.00	50.85	1400.00	213800	3.15	47.95	19.60	0.33	3.27
525-2	0.79	1.85	178.00	57.20	1276.50	192700	4.23	42.33	17.40	0.35	2.56
525-3	0.52	2.14	215.00	69.10	1265.50	175900	4.55	39.48	15.29	0.14	2.12
525-4	3.27	4.81	173.75	53.45	1489.00	230400	3.05	50.63	20.98	0.27	3.16
525-5	2.28	3.27	192.25	58.30	1332.00	183200	4.17	43.05	17.20	0.08	2.36
530-1	0.36	0.51	56.00	15.05	482.50	80900	1.58	18.06	7.48	0.18	1.12
530-2	1.03	0.69	53.00	16.95	415.00	62450	1.56	14.15	5.72	0.11	0.84
530-3	1.84	1.30	26.30	9.35	437.75	88850	3.43	21.34	9.79	0.36	1.67
530-4	0.85	1.07	87.20	23.47	615.00	82500	2.19	1.25	7.35	0.08	1.01
531-1	0.93	0.63	53.15	16.74	423.50	64000	1.46	15.06	6.14	0.16	1.11
610-1	0.86	1.63	147.50	48.90	774.00	96400	1.82	23.07	9.44	0.21	1.35
615-2	1.85	1.57	184.60	56.25	1081.00	137400	1.35	32.42	13.41	0.26	2.00
615-5	3.73	0.54	113.60	30.55	1183.00	178400	0.00	38.45	16.68	0.39	2.82
615-7	1.52	1.69	205.20	64.10	1331.00	186900	0.00	41.30	17.86	0.33	3.27
617-2	0.40	0.66	103.50	30.35	823.00	107800	2.90	26.07	10.47	0.20	1.15
618-1	0.26	1.80	16.58	53.65	943.00	122600	3.32	29.80	12.24	0.25	2.13
618-1	1.06	0.95	117.40	36.00	788.00	109400	2.56	25.93	10.94	0.00	1.75
618-2	3.42	0.51	77.00	20.25	777.00	121200	2.58	28.32	12.07	0.34	2.08
618-3	0.59	1.21	143.40	44.15	948.00	120600	2.88	28.64	12.18	0.36	1.79
618-5	0.45	0.98	138.40	43.90	835.00	114500	3.24	53.66	11.29	0.24	2.42
620-1	0.57	1.44	138.90	44.20	822.50	111750	2.80	26.88	11.10	0.31	1.99
620-3	1.70	3.27	142.20	45.45	863.00	119000	2.80	28.63	11.50	0.45	2.08
621-1	2.58	1.47	140.00	43.85	860.00	124100	3.04	29.54	12.59	0.40	2.19
630-4	2.80	1.60	56.60	16.92	706.00	117600	2.59	28.10	12.16	0.36	2.25
701-1	1.71	1.24	123.40	36.00	868.00	113500	3.42	22.70	11.41	0.00	1.75
701-3	0.20	0.87	131.40	39.00	927.00	129700	3.02	30.64	12.95	0.00	1.94
701-5	2.59	0.96	110.00	32.80	509.00	116800	2.62	27.88	11.77	0.00	2.06
704-1	4.08	4.70	94.20	29.60	864.00	136500	3.91	29.88	12.91	0.00	1.95
704-3	0.30	0.88	130.20	36.20	903.00	123400	2.80	28.60	11.90	0.00	1.89
704-4	0.19	2.57	182.10	60.70	900.00	103900	2.94	23.42	10.05	0.00	1.31
704-6	0.37	1.11	137.80	41.65	827.00	107800	2.72	25.44	10.50	0.00	1.49
705-1	6.89	4.70	75.00	24.05	830.00	130000	3.67	30.10	13.22	0.36	2.25
705-2	0.54	0.59	108.40	34.65	800.00	105200	2.94	24.92	10.38	0.00	1.34
705-3	0.31	0.90	128.60	37.85	904.00	125500	3.10	30.00	12.40	0.00	1.91
618-6	0.71	1.20	112.80	34.05	596.00	80000	1.91	18.58	8.04	0.00	1.20

EXPERIMENTAL DATA FOR THE HEAT GROUP (GROUP B)

Operating Conditions

Identification Number	Rm. Temp. (°C)	Atm. Press. (mm Hg)	Duration of Run (min)	Wt. of Sample (g)	Initial Press. (psig)	Final Press. (psig)	Final Tem. (°C)
519-1	24.0	588.3	6.0	20.00	25	39	109
520-1	24.0	585.7	6.0	23.80	27	55	118
520-2	25.0	584.5	6.0	24.20	29	85	78
520-3	25.0	584.9	6.0	23.90	25	50	109
521-1	24.0	585.9	6.0	23.93	26	64	106
521-2	25.0	585.6	6.0	23.70	26	59	109
522-2	24.5	581.4	6.0	23.82	20	78	68
522-1	24.0	582.1	6.0	23.40	26	56	115
523-1	24.6	586.5	6.0	23.75	26	62	100
523-2	24.5	586.5	6.0	24.10	26	76	79
523-3	24.2	581.1	6.0	23.60	26	59	103
524-1	24.5	589.7	6.0	23.60	25	50	93
524-2	24.7	589.1	6.0	23.42	26	64	95
524-3	24.5	589.0	6.0	23.92	27	75	63
525-1	24.7	588.6	6.0	23.62	26	80	66
525-2	24.7	588.6	6.0	24.51	26	85	82
525-3	24.6	587.7	6.0	22.92	26	75	71
525-4	24.8	587.1	6.0	3.10	18	30	108
525-5	24.5	586.4	6.0	6.00	20	32	107
530-1	24.0	587.8	6.0	24.81	26	82	75
530-2	23.5	587.9	6.0	5.46	20	34	102
530-3	23.8	588.6	6.0	0.71	15	26	104
530-4	23.1	588.9	6.0	5.76	20	32	99
531-1	24.1	588.5	6.0	12.18	23	41	99
610-1	24.1	586.0	6.0	23.43	24	56	47
615-2	24.7	589.3	6.0	23.71	25	65	81
615-5	23.9	588.7	1.5	2.05	19	24	54
615-7	24.1	588.5	1.5	11.92	19	30	45
617-2	23.9	588.5	1.5	4.19	16	23	50
618-1	23.9	588.2	1.5	10.76	19	30	48
618-1	23.9	588.2	1.5	10.76	19	30	48
618-2	23.9	588.4	1.5	3.02	16	22	58
618-3	23.8	588.6	1.5	14.55	20	35	42
618-5	24.0	589.0	1.5	17.98	24	35	40
618-6	24.0	589.0	1.5	21.35	25	37	49
620-1	24.0	587.3	2.5	24.12	24	46	72
620-3	24.0	588.2	2.5	17.58	22	44	55
621-1	23.9	568.8	2.5	13.61	19	37	53
630-4	23.9	587.0	2.5	2.19	15	23	85
701-1	23.2	587.0	2.5	8.39	17	28	74
701-3	23.6	587.0	3.5	24.38	25	60	64
701-5	23.9	586.2	3.5	13.34	19	41	74
704-1	23.9	588.2	3.5	3.75	16	27	98
704-3	23.8	588.3	4.5	23.15	25	62	84
704-4	23.8	588.3	4.5	23.93	25	62	63
704-6	24.8	588.4	5.5	24.40	25	61	66
705-1	23.6	587.8	4.5	3.17	16	28	104
705-2	23.5	587.8	4.5	4.00	16	75	120
705-3	23.6	588.4	4.5	16.30	20	51	71

APPENDIX C

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP C)

EXPERIMENTAL DATA FOR THE CONTROL GROUP (GROUP C)

Chromatographic Data (Peak Areas, cm²)

Identification Number	Methane	Ethane	Propylene	Propane	Isobutane	n-Butane	1-Butene	t-2-Butene	c-2-Butene	n-Pentane	1,3-Butadiene
610-2U	0.00	12.80	162.00	52.30	956.00	116300	1.89	28.19	11.35	0.15	1.28
610-3U	5.24	11.30	121.40	39.50	885.75	112150	1.72	26.88	10.76	0.22	1.50
613-1U	0.96	1.96	170.40	59.10	763.00	86000	1.33	20.10	8.21	0.15	1.26
613-2U	1.19	1.11	141.80	43.15	1007.00	136600	0.32	32.38	13.30	0.20	2.09
613-3U	1.95	1.41	154.80	47.00	932.00	118400	1.46	28.58	11.36	0.08	1.61
614-1U	1.15	0.88	151.20	42.50	1134.50	157900	1.84	38.18	15.72	0.38	2.55
615-2U	10.07	1.45	148.20	47.25	841.00	105600	1.38	25.54	10.70	0.14	1.53
614-3U	1.18	1.48	195.00	64.20	1011.00	120500	1.24	28.68	11.32	0.13	1.64
614-4U	14.60	2.00	89.4	26.00	707.00	97800	2.50	24.03	9.65	0.27	1.28
615-1U	2.12	0.92	145.2	42.65	1020.00	132100	1.32	31.02	12.79	0.16	1.89
615-4U	2.81	0.92	97.40	27.75	959.00	146900	1.64	34.58	15.65	0.25	2.38
615-6U	2.17	0.77	113.00	33.20	884.00	130200	1.52	31.08	13.03	0.69	2.17
617-1U	0.42	1.10	138.10	42.00	900.00	119200	2.76	28.47	11.87	0.21	1.71
617-3U	0.27	0.59	95.20	25.49	809.00	121600	2.71	29.58	12.55	0.40	2.09
617-4U	0.43	1.31	141.00	44.10	844.00	113100	2.89	27.39	11.55	0.28	1.81
617-5U	0.23	1.33	133.40	42.00	804.00	108900	2.64	26.41	10.92	0.28	1.90
617-6U	0.14	1.40	146.80	46.75	873.00	116300	3.13	25.98	11.58	0.25	1.79
617-7U	0.16	2.13	157.00	66.60	870.00	109000	3.15	26.30	10.59	0.21	1.72
621-2U	53.10	212.60	147.40	67.30	947.00	125700	3.48	30.26	12.47	0.00	1.92
623-1U	0.70	1.42	155.00	48.15	756.00	90500	3.05	20.56	8.47	0.00	1.00
623-2U	45.08	43.40	159.40	54.20	811.00	99300	2.52	23.33	9.60	0.20	1.42
628-1U	0.16	0.12	74.82	69.96	757.00	132200	2.29	29.96	13.80	0.55	2.67
628-2U	0.37	1.04	133.80	39.50	864.00	111200	2.92	26.00	10.94	0.23	1.58
628-3U	0.62	0.66	112.40	32.25	839.00	111200	2.65	26.22	10.89	0.22	1.41
628-4U	0.54	0.86	118.80	34.60	839.00	113600	2.91	27.00	11.25	0.22	1.56
628-5U	0.61	1.27	140.60	42.25	739.00	86500	2.16	20.50	8.29	0.09	1.04
628-6U	0.50	7.80	125.40	29.60	875.00	114400	2.95	27.00	11.21	0.00	1.72
628-7U	0.57	2.29	200.90	71.40	951.00	105500	3.38	24.34	9.84	0.10	1.17
629-1U	0.10	0.51	101.80	30.00	861.00	123100	2.89	29.06	12.11	0.38	1.92
629-2U	0.30	1.59	182.60	56.85	1000.00	118000	3.27	28.92	10.54	0.00	1.60
629-3U	0.29	1.02	144.80	42.70	923.00	117700	3.01	27.70	11.92	0.00	1.72
629-4U	0.38	1.56	187.90	65.10	1162.00	131700	3.57	30.56	12.69	0.09	1.68
629-5U	0.40	0.80	77.20	19.75	850.00	130800	2.73	32.30	13.24	0.30	2.23
629-6U	0.41	1.25	158.20	48.00	965.00	123300	3.04	28.26	12.11	0.24	1.68
630-1U	0.24	0.47	97.20	25.95	880.00	124300	2.71	29.12	3.30	0.00	1.98
630-2U	0.29	1.40	180.60	57.60	1000.00	115000	6.79	28.30	10.75	0.00	1.47
630-3U	0.45	2.67	262.00	43.70	983.00	98500	3.15	22.74	9.06	0.00	0.85
630-5U	0.90	0.19	74.60	19.40	813.00	121300	2.68	28.88	12.38	0.22	1.91
701-2U	0.20	1.18	120.00	34.05	882.00	145200	2.78	25.18	10.75	0.00	1.56
701-4U	0.02	2.11	186.90	72.10	877.00	103800	2.77	24.22	9.93	0.00	1.38
701-6U	0.80	0.40	90.20	23.70	877.00	124200	2.73	29.36	12.39	0.00	1.91
701-7U	0.51	1.27	150.50	46.10	867.00	105400	2.81	25.00	10.02	0.00	1.37
704-2U	0.63	1.18	165.80	49.40	953.00	115500	3.02	26.28	10.66	0.11	1.42
704-5U	0.57	2.32	201.00	68.50	807.00	87900	2.79	20.44	7.64	0.00	0.83
705-4U	0.50	1.68	173.00	56.60	740.0	77500	2.41	17.80	6.92	0.00	1.81

EXPERIMENTAL DATA FOR THE ULTRASONIC GROUP (GROUP C)

Operating Conditions

Identification Number	Rm. Temp. (°C)	Atm. Press (mm Hg)	Duration of Run (min)	Weight of Sample (g)	Initial Press. (psig)	Final Press. (psig)	Final Temp. (°C)	Frequency (kHz)	Plate Current (m amp)
610-2U	23.5	585.8	5.0	25.01	26	68	47	26.3	0.9
610-3U	23.6	585.4	5.0	24.39	26	59	47	22.6	1.0
613-1U	23.9	592.6	5.0	24.00	25	50	69	24.5	1.0
613-2U	23.8	592.4	5.0	24.16	25	65	73	22.2	1.0
613-3U	24.6	591.9	5.0	23.95	25	70	79	24.5	1.0
614-1U	25.6	592.5	5.0	23.93	25	70	78	28.1	1.0
614-2U	24.9	591.9	5.0	14.85	20	65	64	27.0	1.0
614-3U	23.9	591.4	5.0	22.11	19	60	77	28.8	1.0
614-4U	24.8	590.9	5.0	5.28	16	50	117	28.4	1.0
615-1U	24.6	588.5	5.0	8.89	19	56	118	27.9	1.0
615-4U	23.0	589.3	5.0	5.75	16	51	85	28.4	1.0
615-6U	24.0	588.5	1.5	7.44	17	35	94	26.5	1.0
617-1U	23.9	588.5	1.5	11.70	18	45	68	28.5	1.0
617-3U	23.1	590.0	1.5	5.56	16	39	68	28.4	1.0
617-4U	24.4	589.6	1.5	14.08	20	51	56	28.0	1.0
617-6U (A)	24.4	589.6	1.5	17.52	21	52	43	27.5	1.1
617-6U (B)	23.9	589.4	1.5	19.97	22	54	39	27.2	1.0
617-7U	24.9	588.7	1.5	23.39	25	57	45	28.0	1.1
621-2U	23.8	586.4	2.5	16.84	20	65	65	27.3	1.0
623-1U	23.6	584.7	2.5	13.89	22	80	84	24.5	1.0
623-2U	23.9	584.5	2.5	20.39	22	79	64	28.5	1.0
628-1U	23.9	588.9	1.5	1.39	17	24	28	29.6	1.0
628-2U	23.4	589.1	1.5	16.63	20	29	25	25.5	1.0
628-3U	24.0	589.4	1.5	5.16	18	34	28	29.5	1.0
628-4U	23.9	590.4	1.5	10.93	19	29	25	25.5	1.0
628-5U	24.0	590.1	2.5	15.55	20	40	29	26.9	1.0
628-6U	24.0	589.7	2.5	7.90	17	36	34	28.3	1.0
628-7U	24.0	590.1	2.5	19.20	25	72	48	30.0	1.0
629-1U	23.9	587.5	3.5	4.62	17	32	29	28.0	1.0
629-2U	23.9	587.6	3.5	19.38	22	49	35	27.0	1.0
629-3U	23.7	587.5	3.5	11.35	18	35	29	28.0	1.0
629-4U	23.5	587.5	4.5	24.86	25	59	40	27.7	1.0
629-5U	24.0	587.5	4.5	3.62	19	52	48	28.0	1.0
629-6U	24.0	586.9	4.5	8.81	21	61	44	27.6	1.0
630-1U	23.2	587.3	6.0	5.06	17	41	41	28.0	1.0
630-2U	23.6	587.0	6.0	17.23	21	52	37	27.8	1.0
630-3U	23.5	586.7	6.0	24.80	25	60	41	27.8	1.0
630-5U	23.5	587.0	2.5	2.68	15	44	126	29.3	1.0
701-2U	23.1	587.0	2.5	8.01	18	50	115	28.1	1.0
701-4U	23.6	587.0	3.5	25.14	25	75	55	27.3	1.0
701-6U	23.9	586.2	3.5	3.80	16	50	121	28.3	1.0
701-7U	23.9	586.2	3.5	3.75	20	75	78	27.2	1.0
704-2U	24.0	588.3	3.5	14.05	20	75	85	27.8	1.0
704-5U	24.5	588.4	5.0	23.91	25	136	82	28.4	1.0
705-4U	23.8	588.3	4.5	13.50	20	110	83	28.2	1.0

VITA

Arnold Harvey Pelofsky

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE EFFECT OF ULTRASONIC ENERGY ON THE PYROLYSIS OF n-BUTANE

Major Field: Chemical Engineering Minor Field: Mathematics

Biographical:

Personal Data: Born in Brooklyn, New York, September 18, 1934, the son of Max and Bertha Pelofsky.

Education: Graduated from Stuyvesant High School in June, 1951; attended Brooklyn College from 1951 to June 1955 and received a Bachelor of Science Degree in June, 1955, with a major in Biology; attended Oklahoma State University from September, 1960 to August, 1964 and in May, 1963 received a Masters of Science Degree, with a major in Chemical Engineering; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in May, 1971.

Professional Experience: U. S. Air Force Officer from August, 1955 to July, 1967; achieved the rank of Major; was a Chemistry Instructor at the U. S. Air Force Academy, Colorado from September, 1964 to July, 1967; Research Chemical Engineer with Cities Service Oil Company from September, 1967 to the present.