

ANALYSIS OF PROPANE EFFLUENT FROM A
DIFFERENTIAL REACTOR USING AN
ULTRASONIC DETECTOR

By

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ARTIFICIAL SWEETENERS

THESE RESULTS WERE OBTAINED FROM A STUDY OF THE EFFECTS OF ARTIFICIAL SWEETENERS ON THE METABOLISM OF CARBOHYDRATES IN THE RAT. THE STUDY WAS CONDUCTED IN THE LABORATORY OF PUBLIC HEALTH, STATE DEPARTMENT OF HEALTH, BOSTON, MASSACHUSETTS, IN 1971.

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ANALYSIS OF PROPANE EFFLUENT FROM A
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ULTRASONIC DETECTOR

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PREFACE

The mechanism of propane pyrolysis is not fully understood and much contradictory data are available in the literature. The ultrasonic detector has been used successfully for trace analyses using helium and oxygen as carrier gases. This study is to evaluate the detector's usefulness in pyrolysis studies using propane as both the feedstock and carrier gas. The reactor was maintained at 517°C and 2 psig.

I acknowledge Dr. B. L. Crynes for serving as my adviser. I thank Ron Johnson for running a mass spectrum on the reactor effluent.

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CHAPTER I

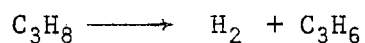
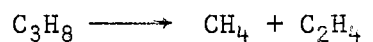
INTRODUCTION

As the chemical processing industry progresses, the trend toward custom products continues. This trend requires special feedstocks other than those occurring naturally. Pyrolysis is one method for converting hydrocarbons to the desired feedstocks. To predict products from pyrolysis reactions which occur over a wide range of operating conditions, a mechanistic reaction model is desirable. Most past pyrolysis studies were either made at sub-atmospheric pressures and low conversions or at atmospheric pressures and high conversions. Since most industrial processes are operated at atmospheric pressure or higher, low pressure data may be of limited value. Data collected at atmospheric pressure but at rather high conversion levels can complicate reaction mechanism studies.

One method of collecting data at low conversions and atmospheric pressure is the use of a differential flow reactor. A differential reactor operates with sufficiently small conversions such that the reaction rate remains essentially constant throughout the reactor. However, a differential reactor requires an analytical technique which is sensitive to very small conversions.

The reaction studied in this work was the pyrolysis of propane. The pyrolysis of propane and propane mixtures is an important industrial process for the production of ethylene and propylene. Although many

studies have been made of this process, a great deal of disagreement still exists about the mechanism and overall order of the reaction. Agreement is generally reached that propane pyrolysis is a free radical reaction and the main products can be represented by the overall reactions:



Essentially equimolar quantities of these products are formed at conversions below 30 per cent.

A special gas chromatograph was used to analyze the reactor effluent. The instrument was a Tracor MT-150 gas chromatograph equipped with an ultrasonic detector. The original objective of this study was to evaluate the usefulness of this chromatograph in pyrolysis studies using reactant as a carrier gas. By directly comparing reactor effluent to unreacted feed, the chromatograph responds only to changes in the feed caused by the reaction.

CHAPTER II

LITERATURE REVIEW

The literature survey is divided into two sections. The first section presents a sample of recent articles on the pyrolysis of propane. The second section presents a brief section on the theory for an ultrasonic detector and a section on previous work which used a Tracor MT-150 gas chromatograph.

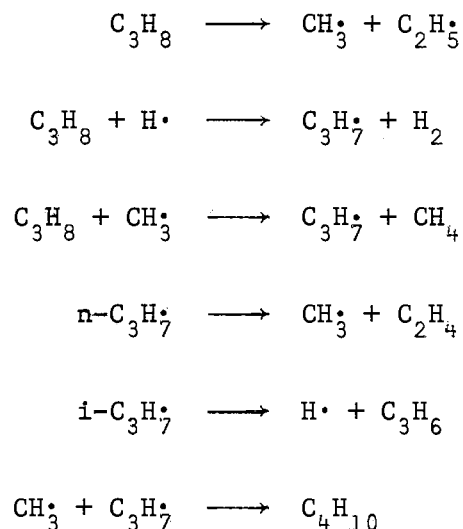
Propane Pyrolysis

Laidler, Sagert, and Wojciechowski (8) have studied the pyrolysis of propane in a quartz batch reactor. The temperature range was 530 to 670°C and the reactor was filled to pressures up to 600 mm Hg. The course of the reaction was followed by measured pressure changes, and the product distributions were reported as partial pressures. The only conversion given was at 570°C and an initial pressure of 212 mm Hg. The conversion was calculated to be 14 per cent and the product distribution was 21 mole per cent hydrogen, 32 mole per cent methane, 5 mole per cent ethane, 22 mole per cent ethylene, and 20 mole percent propylene. The reaction rate decreased by about 20 per cent with an increase in the reactor's surface-to-volume ratio of twelve. The surface-to-volume ratio was increased by packing the reaction vessel with quartz tubing.

A quartz batch reactor was also used by Leathard and Purnell (9) in their propane pyrolysis study. The temperature range was 510 to 560°C with propane consumptions of 0.05 to 2.00 mm Hg at initial pressures between 25 and 260 mm Hg. These pressures could possibly correspond to a conversion range of 0.02 to 8 per cent. Reaction rate was followed by pressure changes. Also the surface-to-volume ratio of the reactor varied from 0.9 to 6.3 cm⁻¹; however, the reaction rate remains constant. This is in contrast to the results reported by Laidler and co-workers. Great efforts were made to remove air from the propane feed since preliminary runs showed that any air present caused the occurrence of abnormally rapid thermal decomposition of the propane. Hydrogen, methane, ethylene, and propylene were formed in equimolar amounts, while ethane was always between 0.3 and 0.9 per cent of the total product yield. "The first run following exposure of a reaction vessel to the atmosphere was also usually abnormally fast, and in such cases detectable amounts of n- and isobutane were occasionally produced."

Buekens and Froment (2) thermally cracked propane in a chromium steel tubular flow reactor. Temperature range was 625 to 850°C and the pressure was atmospheric. The reactor surface was deactivated with carbon disulfide at temperatures between 450 and 550°C. The minimum conversion reported was 2.2 mole per cent at 625°C. Hydrogen, methane, ethylene, and propylene were found to be the primary products, and at low conversions were present in nearly equimolar quantities. Since hydrogen was used as the carrier gas in a chromatographic analysis of the products, the amount of hydrogen had to be calculated by differences from a hydrogen balance.

Free radical mechanisms for the decomposition of propane were proposed by all of the above authors. These mechanisms were all expansions of the model proposed by Rice (12) which is the following:



Crynes and Albright (3) reported the effects of treating the surfaces of stainless steel, low carbon steel, and nickel tubular flow reactors. Reaction temperatures were from 600 to 750°C and pressure was essentially one atmosphere. Hydrogen sulfide and sulfur treatments were found to deactivate the reactor walls by forming a protective metal sulfide film. At low conversions essentially equimolar amounts of hydrogen, methane, ethylene, and propylene were reported. As conversion increased to 37 per cent, concentrations of methane and ethylene increased more rapidly than those of propylene and hydrogen. A minimum conversion of 3 per cent was reported at 650°C.

These articles are by no means intended to be a complete literature survey, but are intended only to indicate the type of work done recently in this field. Other recent work has been done by Sieck, Blocker, and Furtell (14), Kunugi, Tominaga, Abiko, and Namatame (7), Benson (1), Kershenbaum and Martin (6), and Martin and Niclause (10).

Ultrasonic Detectors

F. W. Nobel has pioneered the application of an ultrasonic detector to gas chromatography. In 1964, Nobel, Abel, and Cook (11) presented the theory and instrumentation for an ultrasonic detector. The relation for the phase delay of a sound wave is given first for a pure gas and then for a binary gas mixture.

The time required for a sound to travel a distance, S , at a velocity, V , is

$$t = \frac{S}{V} \quad (1)$$

The phase delay in electrical degrees corresponding to t is

$$\phi = \frac{360 fS}{V} \quad (2)$$

where f is the frequency of the wave in cycles per second. For a pure ideal gas at low frequency

$$V = \left(\frac{rRT}{M}\right)^{1/2} \quad (3)$$

where M = molecular weight

r = ratio of specific heat at constant pressure to the specific heat at constant volume

R = universal gas constant (8.314 joule/mole/°K)

T = absolute temperature.

Combining Equations 2 and 3, one obtains

$$\phi = \frac{360 Sf}{(RT)^{1/2}} \left(\frac{M}{r}\right) \quad (4)$$

For a binary gas mixture this equation is shown to be

$$\phi = \frac{360 Sf}{(RT)^{\frac{1}{2}}} \left(\frac{M_1}{r_1}\right)^{\frac{1}{2}} \left\{1 + \frac{n}{2} \left[\left(\frac{M_2}{M_1} - 1\right) + \frac{C_{p2}}{C_{p1}} \left(\frac{r_1}{r_2} - 1\right)\right]\right\} \quad (5)$$

where the subscript 1 refers to the carrier gas and 2 to the sample gas, n is the mole fraction of the sample gas, C_p is the specific heat capacity of the gases at constant pressure. This equation assumes that both gases are ideal and that the gas mixture is homogeneous. Also the value of n is assumed to be small. The phase change, $\Delta\phi$, caused by adding the sample gas 2 is given by

$$\Delta\phi = 180 Sf \left[\frac{M_1}{RT r_1}\right]^{\frac{1}{2}} n \times \left[\left(\frac{M_2}{M_1} - 1\right) + \frac{C_{p2}}{C_{p1}} \left(\frac{r_1}{r_2} - 1\right)\right] \quad (6)$$

Equation 6 predicts that a sample gas with a molecular weight less than the carrier gas will give a positive phase response. Equation 6 is valid when the specific heats at the frequency of the sound wave are the same as the tabulated values determined by calorimetry. At high frequencies these tabulated values will generally be valid only for monatomic gases. A prototype instrument was constructed and tested using hydrogen, helium, argon, nitrogen, carbon dioxide, methane, and ammonia as carrier gases.

Grice and David (4) have studied the Tracor MT-150 gas chromatograph equipped with an ultrasonic detector. Carrier gases used were hydrogen, helium, nitrogen, oxygen, air, and argon. Linear responses were observed over the entire range of responses. When using argon as a carrier gas, oxygen and methyl alcohol gave negative responses although they had molecular weights less than the carrier gas. No explanation was offered for this anomaly. Impure carrier gas was found to cause baseline instability and decreased sensitivity. Trace analyses were run on breathing oxygen using purified oxygen as the carrier gas.

and also on grade A helium using helium which had passed through a diffusion furnace as the carrier gas. In such studies, 10 cc gas samples were injected routinely, allowing trace analyses at parts per billion. Todd and DeBord (16) have presented a similar article on a newer model of the MT-150 gas chromatograph.

Kate and Robinson (5) have used an MT-150 gas chromatograph to analyze the vapor phase composition in their solid-vapor equilibrium studies of helium-krypton and helium-xenon systems.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

A flow sheet is shown in Figure 1. The gas flow was controlled with a Nupro valve (A). The flow rate was monitored using a Matheson 620 flowmeter (B). After the reactor the flow rate was measured using a bubble meter. The pressure was maintained at a constant 2 psig in the rotameter by adjusting a Nupro valve (C). A Matheson pressure gauge was used to measure the pressure. After leaving the reactor the gas was passed through a glass-wool trap (D) and a cold trap (E) which was maintained at 0°C. A tee (F) allowed known gases to be added to the reactor effluent before entering the sample loop. These gases were added to the reactor effluent before entering the sample loop. These gases were added for identification purposes. The sample loop was 10.8 feet of 1/16-inch O.D. tubing. The inside diameter of the tubing was 0.030 inches and the volume was calculated to be 1.5 cubic centimeters.

The propane used was Phillips Instrument Grade having a 99.5 mole per cent minimum purity. The specifications listed in the Phillips catalog are 99.6% propane, 0.35% isobutane, and 0.15% n-butane. For two preliminary runs Phillips Research Grade (Lot No. 1136) propane was used. The purity was 99.97% propane with the most probable impurity being ethane. Helium used for purge gas was 99.9995%. All other gases used were more than 90% pure.

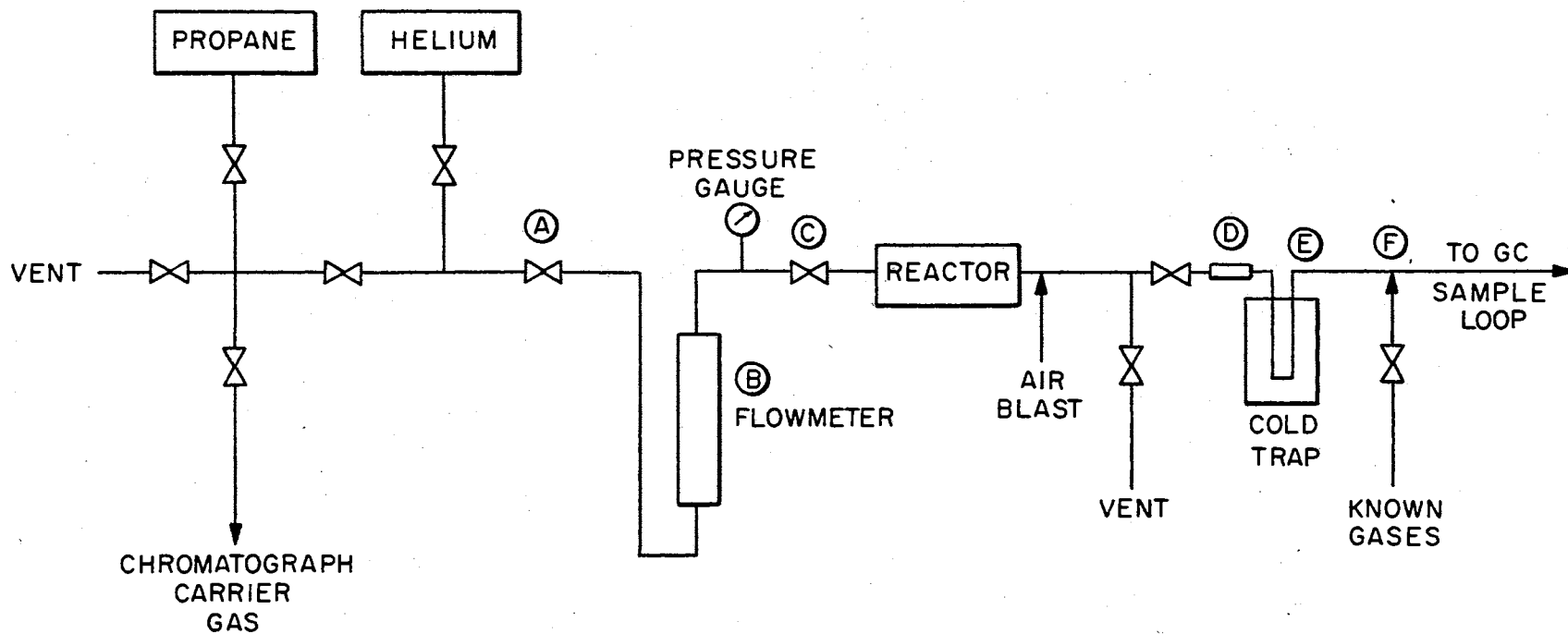


Figure 1. Flow Sheet

Three reactors were constructed. The first reactor had two exit ports, one in the middle of its length and one at the end. The middle port allowed shorter residence times without changing flow rates. This port caused a large heat loss in the middle of the reactor and made controlling the temperature profile extremely difficult. Thus a second reactor was built omitting the center port. An unexpected product was obtained and a third reactor was constructed to check if this product was caused by an impurity in the second reactor.

The final reactor constructed is shown in Figure 2. The reactor was constructed by placing a 1/8-inch O.D. tube inside a 1/4-inch O.D. tube. The tubing walls were 0.035 inches thick. The propane flowed through the annulus which was 0.0275 inches wide. The reactor was 17.9 inches long. All fittings were Swagelok. All material was 316 stainless steel. The reactor was heated by a main heater and secondary heaters on each end to minimize end effects. The beaded heaters had an output of 30 watts per foot at 115 volts. The main heater was approximately three feet long and the secondary heaters were approximately six inches long. About a one inch thickness of fiber glass tape was wrapped around the reactor for insulation. Reactor effluent was immediately cooled by a blast of expanding compressed air.

The voltage was supplied to the heaters by four variacs as shown in Figure 3. The three secondary variacs were connected to the main variac to give more sensitivity in the control of the voltage to the heaters. The primary and secondary variacs were, respectively, Powerstats 136 and 116. The reactor was brought up to reaction temperature by placing the secondary variacs at the desired settings and slowly increasing the output of the main variac to the desired level. Once the

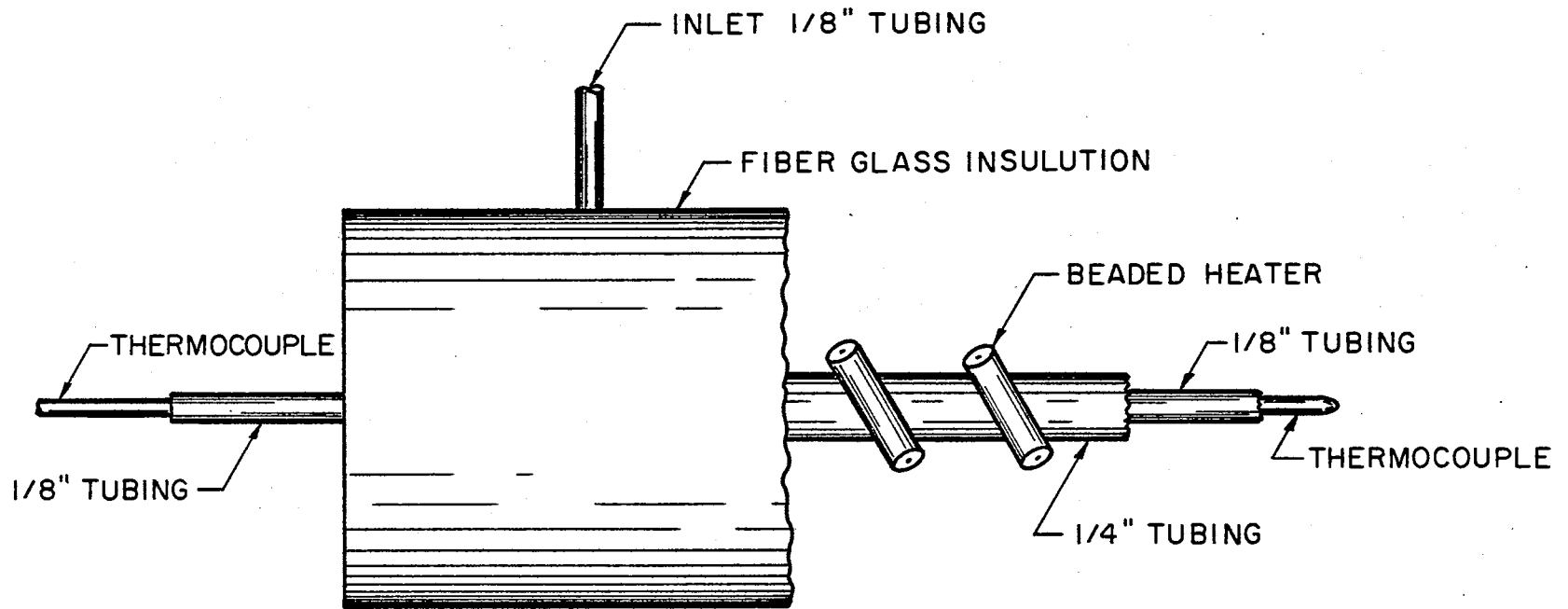


Figure 2. Cutaway View of the Reactor

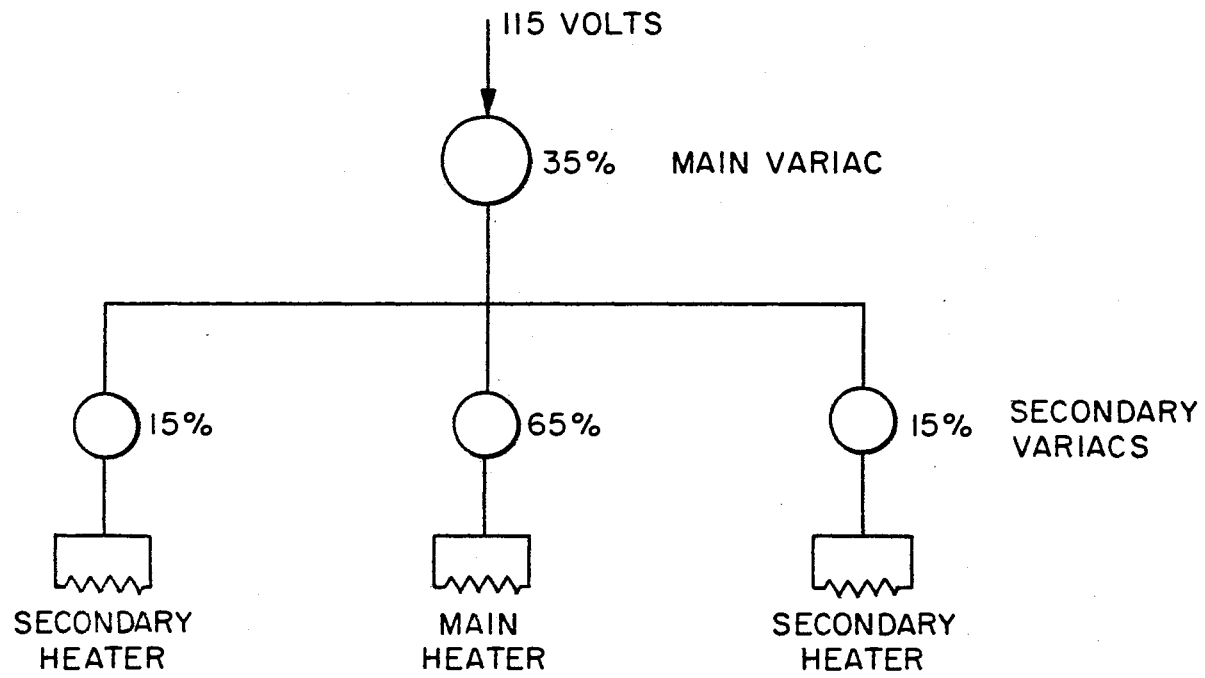


Figure 3. Power Supply to Heaters

reactor was heated to the reaction temperature, it was not cooled down until all data had been taken. Whenever propane was not flowing through the reactor, helium was used to flush the propane out of the reactor, and then a low flow rate of helium was maintained afterwards for a continuous purge.

Temperature measurements were made using a Leeds and Northrup 8686 potentiometer and a Conax K-SS4-G-T3 chromel-alumel thermocouple. The thermocouple was slid along inside the 1/8-inch tube by hand and readings were taken every two centimeters.

A flat temperature profile along the length of the reactor was approached by adjusting the output of the variacs, and also by varying the amount of insulation along the length of the reactor. The profile measured during the final runs is shown in Figure 4.

To reduce catalytic effects of the reactor walls, the reactor was treated with hydrogen sulfide. The reactor was heated to 550°C and hydrogen sulfide was flowed through the reactor for approximately one minute. The reactor was burned out for thirty minutes with compressed air at 600°C before making the final runs.

The reactor effluent was analyzed using an MT-150 gas chromatograph equipped with an ultrasonic detector. Propane was used as the carrier gas during all analyses. This was the same purity of propane used for reactor feed.

The detector system had two identical cells, A and B. The carrier gas flowed through cell B to produce the reference signal and the carrier plus sample flowed through cell A. The detector was operated differentially, i.e., the output signal is the difference of the phase delays in cell A and in cell B. Normally, the differential mode is A

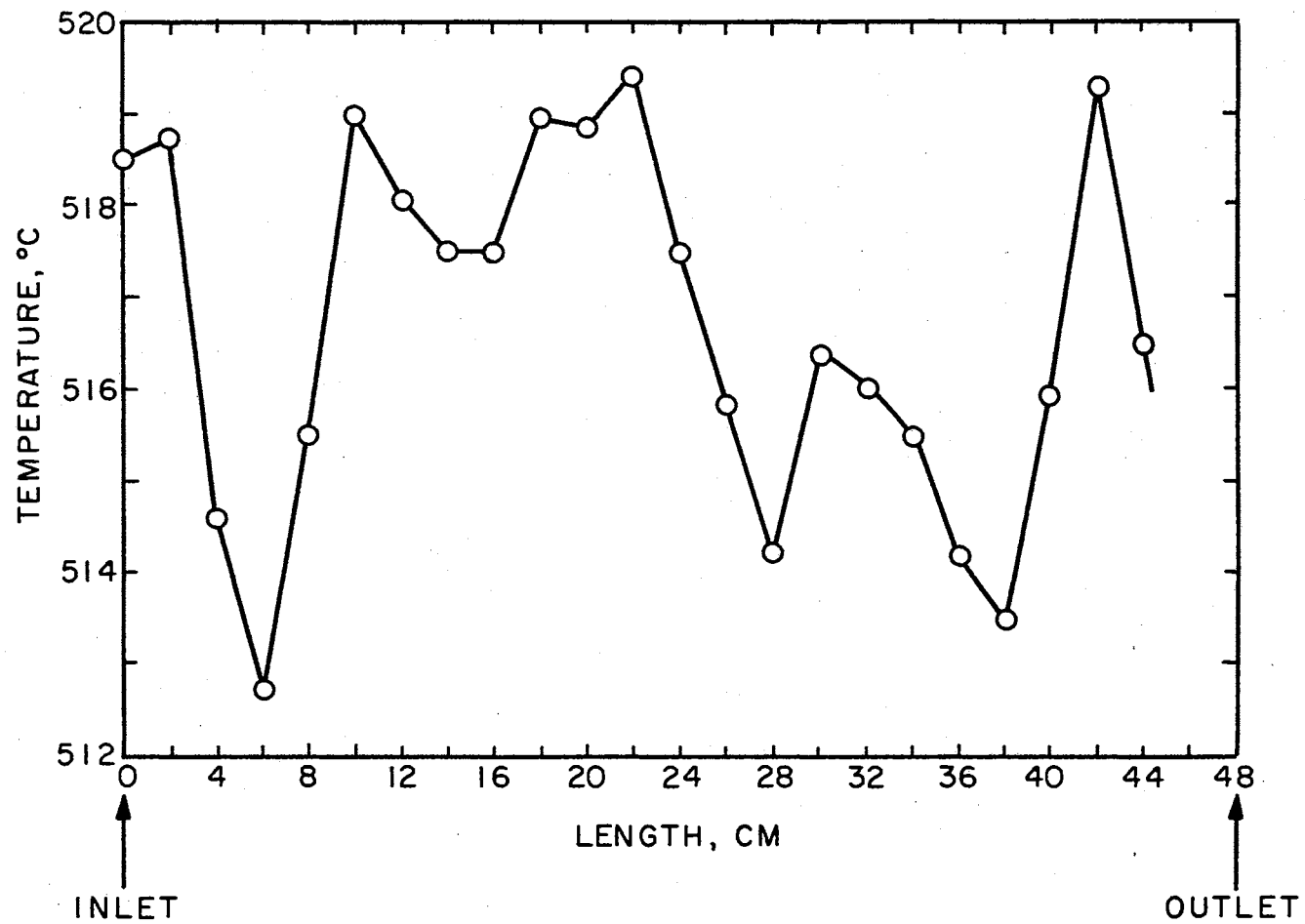


Figure 4. Temperature Profile in the Reactor

minus B, but since the expected products are lighter than the propane carrier gas, the input jacks to the detector were reversed and thus the differential mode was B minus A.

Each cell contained transmitting and receiving transducers. The ceramic transducers were gold-plated and mounted one centimeter apart. They were driven at a fixed frequency of six megacycles. These features are standard on the MT-150 gas chromatograph.

The flow rate through each cell was 30 cc/min. The column temperature was 40°C. The detector temperature was 125°C. The initial phase angle was 16 degrees. The output attenuation of the detector was four.

The chromatograph output was integrated using a Nester/Faust 1504 Summatic integrator equipped with a baseline compensator. The output was recorded by a Honeywell model 15307856-01-05-0-000-715-07 009 recorder.

The chromatographic columns used were a 1/8 inch by 21.3 foot column packed with 120/150 mesh Porapak R followed by a 1/8 inch by 6 foot column packed with 50/80 mesh Porapak Q to separate the sample going to cell A and a 1/8 inch by 21.3 foot column packed with 120/150 mesh porapak R in the stream going to cell B to balance the pressure drop in the two streams thus allowing better flow control. There is no special reason for the Porapak Q-R combination. Porapak is porous polymer beads developed by O. L. Hollis of the Dow Chemical Company.

The response of the chromatograph was calibrated by injecting a known sample of gas and measuring the response. A Micro Tek 712100 two-microliter sampling valve was used to inject the gas samples. The flow through the sample valve was so low that it would barely bubble

when the exit line was placed just below water. The valve was at room temperature and the pressure in valve was at 15 inches of Hg of vacuum. The areas measured are shown in Table I. The mean response for each

TABLE I
 RESPONSES OF KNOWN SAMPLES
 2 Microliter Sample at 15 Inches of Hg Vacuum and 78°F
 Attenuation: 16
 mv · sec

Duplicate No.	Hydrogen	Methane	Ethylene	Ethane	Propylene
1	3200	2058	1252	1083	167
2	3209	2030	1242	1074	168
3	3067	2072	1249	1010	
4		2111	1229		
Mean	3159	2068	1243	1052	
Deviation	79.5	33.7	10.2	33.1	

component was fitted to a straight line through the origin on a plot of response versus moles of gas. A plot of measured response versus molecular weight is shown in Figure 5.

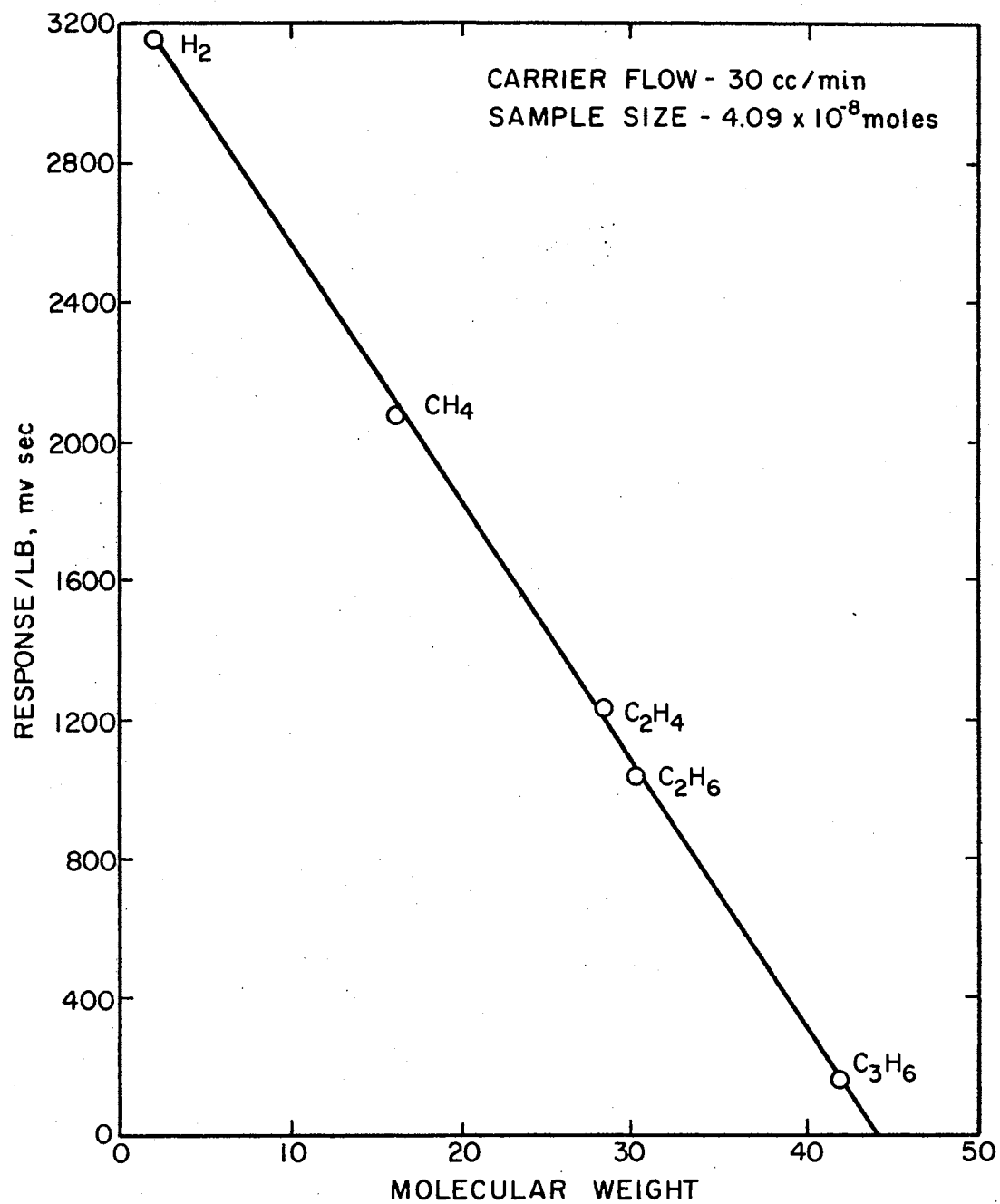


Figure 5. Response vs. Molecular Weight

CHAPTER IV

RESULTS

Twelve runs were made. The mean temperature was calculated from Figure 4 to be 517°C and the pressure was 2 psig. The propane flow rate through the reactor was 40 cc/min. measured at 2 psig and 25°C which gave a residence time of 1.8 seconds. The Reynolds number was 12.5, thus laminar flow existed. Seven negative peaks appeared on the chromatograms. A typical chromatogram is shown in Figure 6. The peaks correspond to a pressure upset, hydrogen, methane, ethylene, ethane, propylene, and a seventh peak. The peaks were identified by adding each one of the expected products to the reactor effluent, one at a time, and noting which peak increased in size. Note that the seventh peak is the largest peak on the chromatogram.

The following were attempts to identify this seventh peak.

(1) The reactor was bypassed and a sample taken. The only peak observed was the pressure upset, therefore the peak must have been produced in the reactor and was not a line impurity which could possibly have accumulated in the traps or elsewhere within the system.

(2) The seventh peak was observed before and after the reactor walls were treated with hydrogen sulfide and before and after the reactor was burned out with air. Thus, the peak was present with several reactor wall conditions: plain stainless steel, a sulfide surface, and highly oxidized by burn out.

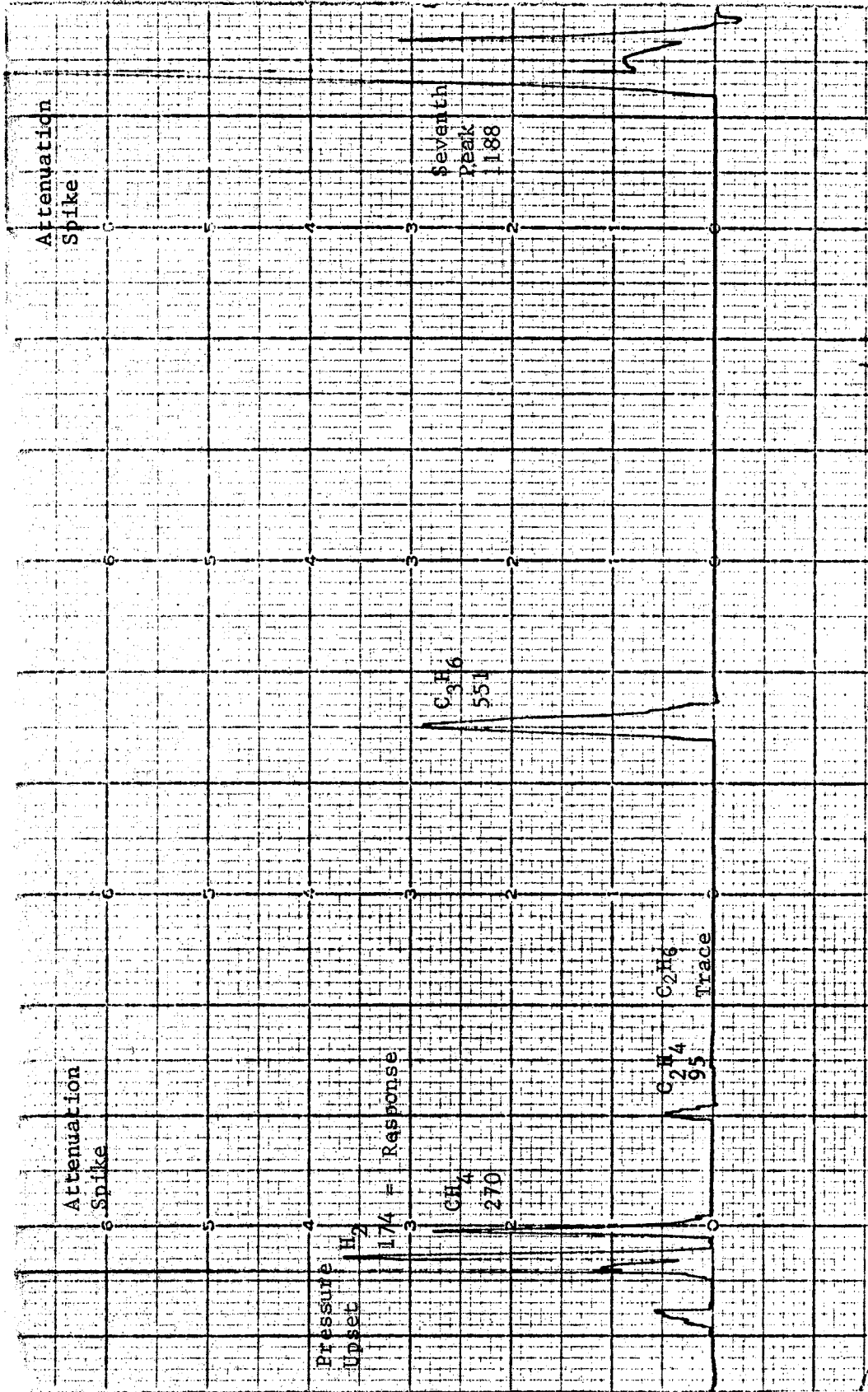


Figure 6. Sample Chromatogram

(3) The reactor temperature was increased to 700°C which increased the conversion to roughly 25 per cent. All the peaks increased in size except the pressure upset and the seventh peak. Thus the seventh peak was insensitive to conversion.

(4) When research grade propane was used for two runs, the seventh peak was still present. Apparently, the peak was not from an impurity in the instrument grade propane.

(5) Several gases were added to the reactor effluent in an effort to identify the seventh peak. Acetylene, methyl acetylene, allene, cyclopropane, carbon dioxide, and hydrogen sulfide all appeared before the seventh peak as did water, which was added to the reactor effluent by bubbling the gas through water in the cold trap.

(6) A mass spectrograph was made of the reactor effluent on a LKB 9000 combination gas chromatograph-mass spectrometer. The only peak detected after the propane peak was isobutane. However, when isobutane was added to the reactor effluent before sampling, a positive peak appeared where the seventh peak had been. The unknown peak had negative response.

Propane conversion, excluding the seventh peak, ranged from 0.030 per cent to 0.060 per cent. The hydrogen-to-carbon atom ratio ranged from 2.02 to 2.07. Complete product distributions are given in Table II.

TABLE II
PRODUCT DISTRIBUTIONS

Run No.	Mole Per Cent					Propane Conversion %	H/C Atom Ratio
	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆		
11-3-7	0.00100	0.00427	0.00444	0.00000	0.10947	0.0596	2.03
11-3-8	0.00095	0.00458	0.00149	0.00017	0.08517	0.0462	2.04
11-3-9	0.00177	0.00521	0.00221	0.00000	0.06933	0.0393	2.06
11-3-10	0.00114	0.00557	0.00318	0.00060	0.06664	0.0386	2.07
11-3-11	0.00080	0.00372	0.00273	0.00062	0.07272	0.0403	2.07
11-3-12	0.00184	0.00512	0.00122	0.00014	0.06933	0.0388	2.07
11-3-13	0.00111	0.00524	0.00319	0.00000	0.09035	0.0500	2.04
11-3-14	0.00097	0.00588	0.00416	0.00000	0.08049	0.0458	2.05
11-3-15	0.00130	0.00192	0.00932	0.00000	0.05296	0.0326	2.04
11-3-16	0.00092	0.00217	0.00127	0.00000	0.05489	0.0296	2.04
11-3-17	0.00050	0.00171	0.00201	0.00000	0.07262	0.0384	2.02
11-3-18	0.00044	0.00160	0.00125	0.00000	0.06784	0.0356	2.02
Mean	0.00106	0.00392	0.00304	0.00013	0.07429	0.0412	2.04
Devi- ation	0.00043	0.00163	0.00227	0.00023	0.01552	0.0081	0.02

CHAPTER V

DISCUSSION OF RESULTS

The lack of reproducibility of the conversion which was 0.041 ± 0.008 per cent may be primarily caused by fluctuations of the reactor temperature profile. A secondary effect was a varying pressure in the sample loop causing a slightly different volume of sample gas to be injected. The methane/propylene ratio was 0.053 ± 0.021 and the ethylene/propylene ratio was 0.044 ± 0.043 . This variation in the product distribution is largely due to errors in the integration of the areas of the peaks.

An annular reactor has previously been used in propane pyrolysis studies. Kershenbaum and Martin (6) experimentally checked the reading of a thermocouple in the center core of an annular reactor with a thermocouple placed in the annulus space. Over a wide range of flows and temperatures the two thermocouples agreed within 3°C . Also, Robinson (13) calculated that the thermowell wall would be 4°C higher than the actual gas temperature for a propylene pyrolysis study at 1100°C . Since this work fell within the range studied, the gas temperature was very likely within 4°C of the measured temperature. All temperatures measured along the length of the reactor were within 4°C of the mean of 517°C .

The propylene reaction seems to be highly favored over the methane-ethylene reaction. This is in direct contradiction of the popular belief that the two reactions proceed at approximately the same rates.

The conversion of 0.041 per cent observed in this work is higher than one would expect from the results of earlier works. Using the activation energies and frequency factors reported by Laidler et al (8) and by Steacie and Puddington (15) conversions of 0.010 per cent and 0.014 per cent, respectively, were calculated. The temperature ranges studied were 530-670°C for Laidler and 551-602°C for Steacie. Both works were done at low pressure in quartz batch reactors and at higher conversions.

If the seventh peak is indeed isobutane as the mass spectrograph indicated, then the response of isobutane must be highly non-ideal since it gives a negative peak at very low concentrations and a positive peak at higher concentrations. Non-ideal responses were noted by Grice and David (4) when using argon as a carrier gas and oxygen and methyl alcohol gave positive peaks although their molecular weights were less than the molecular weight of argon.

Butane has been produced by Whitten and Rubinovitch (17) by adding diazomethane to propane and activating the mixture with light at room temperature. However, the amount of n-butane formed was 2.5 times the amount of isobutane formed. The butanes were formed by the insertion of the methylene radical produced from the diazomethane into propane. As mentioned above, butane was found by Leathard and Purnell (9) when their reaction vessel had been exposed to the atmosphere.

The hydrogen-to-carbon ratio for the reactor effluent should be 2.67, that of propane, instead of the 2.04 reported. Having isobutane present would increase the H/C ratio slightly toward 2.5. The low H/C ratio indicates that some hydrogen is missing. I feel that the missing hydrogen may be in the form of water which is eluted from the column so

slowly that the peak is not observed on the chromatogram. When testing for the identity of the seventh peak with water vapor, the water peak eluted very slowly. Less than 200 parts per million of oxygen would be required to be present in the feed to produce the amount of water necessary to account for the missing hydrogen.

The conversions obtained in this study were the lowest possible and still maintain a detectable ethane peak. An increase in sample size to 11.5 cc to allow for even lower conversions caused a large pressure upset that obscured the hydrogen peak. If the sample were prepressurized, the pressure upset would be minimized and thus allow a larger sample size. This was not tried, however. Also the attenuation was set at four to reduce the baseline noise. The baseline noise could be reduced by purifying the propane carrier gas and thus allow the chromatograph to operate at a more sensitive attenuation.

Since the seventh peak did not appear when the sample stream bypassed the reactor, the peak must correspond to a reaction product or some impurity in the reactor. Therefore a new reactor was built, but the seventh peak still appeared. The peak did not decrease during the month that the reactor was kept at reaction temperature, thus it could not be an impurity or conditioning effect. Therefore the seventh peak must be a reaction product.

The temperature of the reactor was increased to approximately 700°C which increased the conversion to roughly 25 per cent. All peaks increased significantly in size except the pressure peak and the seventh peak, which indicates that the size of the seventh peak is insensitive to conversion. Although the 25 per cent conversion range has been studied before, the seventh is a minor product (approximately 0.2 per

cent of the total product) at these conditions and could have been overlooked by earlier workers. If the seventh peak were an intermediate in the reaction scheme, the peak could reach its maximum size and then be relatively insensitive to conversion.

The peak was also the same size before and after treating the reactor walls with hydrogen sulfide. Using research grade propane for both feedstock and carrier gas did not affect the size of the seventh peak either. Thus, within the region tested wall activity and feedstock purity did not affect the size of the seventh peak.

Although the method of chromatograph response calibration may not be extremely accurate, about the same error should be present in each component. Thus, the ratio of components should be accurate.

A fairly flat temperature profile was obtained; however, better methods of heating the reactor can be developed. The present reactor took a long period of time to reach steady state and required a great amount of adjusting to obtain a relative flat temperature profile.

CHAPTER VI

CONCLUSIONS AND RECOMENDATIONS

The ultrasonic detector can provide a very sensitive analytical tool which will respond to all gases other than the carrier. By using the sample matrix as the carrier gas, large samples can be analyzed which allows trace analyses. This concept is very useful in pyrolysis studies and should be utilized in future pyrolysis studies, especially when low conversions are desired for mechanistic studies.

The advantages of using propane as the carrier gas are the following:

- (1) Large sample sizes are allowed without flooding the column.
- (2) Propylene need not be separated from propane.
- (3) The large propane peak, which would probably be off scale when using a carrier gas such as helium, is not observed.
- (4) The propane peak might smother other peaks which would elude during the same time interval.

The major disadvantage for using propane as a carrier gas is that no convenient method such as a diffusion furnace is available for purifying propane. Thus, such studies must be limited to research grade stock or tedious additional purification steps must be taken.

Although not shown conclusively, I feel that the seventh peak is isobutane and that isobutane gives a non-ideal response. Also isobutane is an intermediate in the decomposition scheme and the observed

concentration is a steady-state concentration. This development should indeed be investigated in the future.

For future work I offer the following recommendations:

(1) Purify the propane used, possibly by degassing it with liquid nitrogen.

(2) Calibrate the chromatograph using dilute propane mixtures of known compositions.

(3) Pre-pressurize the sample to carrier gas pressure before injecting the sample.

(4) Use a hot metal block to supply the main heat source for the reactor with secondary heating coils on the ends to minimize end effects. The metal block would simplify maintaining a flat temperature profile along the length of the reactor.

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APPENDIX A

TYPICAL CALCULATIONS

APPENDIX A

TYPICAL CALCULATIONS

Ideal gas behavior was assumed in all calculations.

Calculation of Residence Time

$$\text{Flow rate at } 25^{\circ}\text{C and } 2 \text{ psig: } F_1 = 40 \frac{\text{cc}}{\text{min}} = 0.67 \frac{\text{cc}}{\text{sec}}$$

$$\text{From Charles' Law: } F_2 = F_1 * \frac{T_2}{T_1}$$

at 790°K

$$F_2 = 0.67 \frac{\text{cc}}{\text{sec}} * \frac{790^{\circ}\text{K}}{298^{\circ}\text{K}} = 1.768 \frac{\text{cc}}{\text{sec}}$$

$$\text{Volume of reactor: } V = \frac{\pi}{4} (D_0^2 - D_1^2) * L$$

$$V = \frac{\pi}{4} (0.180^2 - 0.125^2) \text{in}^2 * 14.69 \text{ in} = 0.1938 \text{ in}^3$$

$$= 0.1938 \text{ in}^3 * \frac{16.39 \text{ cc}}{\text{in}^3} = 3.18 \text{ cc}$$

$$\text{Residence time: } t = \frac{V}{F}$$

$$t = \frac{3.18 \text{ cc}}{1.768 \text{ cc/sec}} = 1.8 \text{ sec}$$

Calculation of Conversion from Experimental Results

Data from Run 11-3-10:

<u>Component</u>	<u>Area</u>	Attenuation = 4
H ₂	216	Sample size = 1.5 cc at 25°C
CH ₄	693	= 6.14 x 10 ⁻⁵ g mole
C ₂ H ₄	237	
C ₂ H ₆	38	
C ₃ H ₆	669	

$$\text{Area}_i * \text{Att} = K_i * \text{Moles}_i$$

where K_i is the GC calibration factor.

$$\text{From calibration data: } K_{\text{H}_2} = 123.5 \times 10^{10} \frac{\text{deg sec}}{\text{gm mole}}$$

$$K_{\text{CH}_4} = 81.0 \times 10^{10}$$

$$K_{\text{C}_2\text{H}_4} = 48.6 \times 10^{10}$$

$$K_{\text{C}_2\text{H}_6} = 41.2 \times 10^{10}$$

$$K_{\text{C}_3\text{H}_6} = 6.54 \times 10^{10}$$

$$\text{Moles}_i = \frac{\text{Area}_i * \text{Att}}{K_i}$$

	<u>Moles</u>	<u>Mole per cent</u>
H ₂ : moles = $\frac{216 * 4}{123 \times 10^{10}} =$	7.0 x 10 ⁻¹⁰	0.00114
CH ₄ : = $\frac{693 * 4}{81 \times 10^{10}} =$	34.2 x 10 ⁻¹⁰	0.00558
C ₂ H ₄ : = $\frac{237 * 4}{48.6 \times 10^{10}} =$	19.5 x 10 ⁻¹⁰	0.00318

$$C_2H_6: \quad = \frac{38 * 4}{41.2 * 10^{10}} = 3.68 * 10^{-10} \quad 0.00060$$

$$C_3H_6: \quad = \frac{669 * 4}{6.54 * 10^{10}} = \frac{409.0 * 10^{-10}}{473.38 * 10^{-10}} \quad 0.06600$$

To calculate conversion the following nomenclature was used.

R_C = moles of reactant converted to product

R_S = moles of reactant in a sample

P = moles of product in a sample

E = moles of product formed from one mole of reactant,
being completely converted.

S = moles in a sample.

Then

$$\text{Conversion} = \frac{R_C}{R_S} = \frac{P/E}{S - P/E}$$

Assuming E is two, we obtain

$$\text{Conversion} = \frac{\frac{4.734 * 10^{-8}}{2}}{6.14 * 10^{-5} - \frac{4.734 * 10^{-8}}{2}} = 3.86 * 10^{-4} = 0.0386\%$$

Calculation of Conversion from Literature Rate Constants

For a first order reaction with one mole of reactant yielding two moles of product,

$$k\tau = -\chi - 2.0 * \ln(1 - \chi)$$

For small conversions

$$k\tau \approx \chi$$

The residence time, t , is 1.8 seconds.

Laidler et al (8) report that

$$k = 2.58 \times 10^{14} \exp(-67100/RT)$$

$$k_{790} = 2.58 \times 10^{14} \exp\left(\frac{-67100}{1.987 \times 790}\right) = 5.7 \times 10^{-5} \text{sec}^{-1}$$

$$kt = 5.7 \times 10^{-5} \text{sec}^{-1} * 1.8 \text{ sec} = 1.025 \times 10^{-4} = 0.0102\%$$

Sheacie and Puddington (15) report that

$$k = 2.88 \times 10^{13} \exp(-63300/RT)$$

$$k_{790} = 2.88 \times 10^{13} \exp\left(\frac{-63300}{1.986 \times 790}\right) = 7.77 \times 10^{-5} \text{sec}^{-1}$$

$$kt = 7.77 \times 10^{-5} \text{sec}^{-1} * 1.8 \text{ sec} = 1.40 \times 10^{-4} = 0.0140\%$$

To calculate conversion from rate constants the following nomenclature was used.

t = residence time, sec

T = space time, sec

k = rate constant, sec

X = fractional conversion

APPENDIX B

THEORETICAL RESPONSES OF CALIBRATION GASES

APPENDIX B

THEORETICAL RESPONSES OF CALIBRATION GASES

From Equation 6 we know

$$\Delta\phi = 180 \text{ Sf} \left[\frac{M_1}{RT r_1} \right]^{1/2} \cdot n \cdot \left[\left(\frac{M_2}{M_1} - 1 \right) + \frac{C_{p2}}{C_{p1}} \left(\frac{r_1}{r_2} - 1 \right) \right]$$

The response area, A_2 , is

$$A_2 = \Delta\phi \cdot \frac{\text{mv}}{0.36 \text{ deg}}$$

The mole fraction, n , is

$$n = \frac{N_2 RT}{PF}$$

where N_2 = number of moles of sample

P = pressure

F = flow rate of the carrier gas.

Combining,

$$A_2 = 180 \cdot \text{Sf} \left[\frac{M_1 RT}{r_1} \right]^{1/2} \frac{N_2}{PF} \left[\left(\frac{M_2}{M_1} - 1 \right) + \frac{C_{p2}}{C_{p1}} \left(\frac{r_1}{r_2} - 1 \right) \right] \frac{\text{mv}}{0.36 \text{ deg}}$$

$$A_{H_2} = \frac{360 \text{ deg}}{2 \text{ cycle}} \cdot 1 \text{ cm}$$

$$\cdot 6 \times 10^6 \frac{\text{cycle}}{\text{sec}} \left[\frac{44 \text{ gm}}{\text{mole}} \cdot \frac{3.314 \times 10^7 \text{ erg}}{^\circ\text{K mole}} \cdot \frac{398^\circ\text{K}}{1.13} \right]^{1/2}$$

$$\cdot \frac{4.09 \times 10^{-8} \text{ moles}}{33 \text{ psig} \cdot 6.895 \times 10^4 \frac{\text{dyne}}{\text{cm}^2} \cdot \text{psig}} \cdot 0.5 \frac{\text{cc}}{\text{sec}}$$

$$\left[\frac{2}{44} - 1 \right] + \frac{6.944}{22.478} \left(\frac{1.13}{1.40} - 1 \right) \frac{\text{mv}}{0.36 \text{ deg}}$$

$$A_{H_2} = 120.0 [-1.0143] \text{ mv} \cdot \text{sec} = -122 \text{ mv} \cdot \text{sec}$$

$$A_{CH_4} = 120.0 [-0.6692] \text{ mv} \cdot \text{sec} = -80.5 \text{ mv} \cdot \text{sec}$$

$$A_{C_2H_4} = 120.0 [-0.4060] \text{ mv} \cdot \text{sec} = -49.5 \text{ mv} \cdot \text{sec}$$

$$A_{C_2H_6} = 120.0 [-0.3686] \text{ mv} \cdot \text{sec} = -44.4 \text{ mv} \cdot \text{sec}$$

$$A_{C_3H_6} = 120.0 [-0.0365] \text{ mv} \cdot \text{sec} = -4.39 \text{ mv} \cdot \text{sec}$$

Table III presents experimental and calculated responses for expected products.

TABLE III. EXPERIMENTAL AND CALCULATED RESPONSES FOR EXPECTED PRODUCTS

Component	Experimental (E)	Calculated (C)	E/C
H ₂	-50,500	-122.0	414
CH ₄	-33,100	-80.5	411
C ₂ H ₄	-19,900	-49.5	403
C ₂ H ₆	-16,850	-44.4	380
C ₃ H ₆	-2,680	-4.39	611

Although the experimental responses and the calculated responses are not in agreement, the ratio of experimental to calculated values are approximately except for propylene.

VITA

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