



Coal hydrogenation studies using a $\text{KCl} - \text{ZnCl}_2$ molten salt mixture as a catalyst
by John Sebastian Malsam

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

Previous research by Consolidation Coal Company had shown that zinc chloride was a superior catalyst for the hydrogenation of coal and coal extract. It gave rapid conversion to predominantly gasoline range liquids at low temperatures and pressure. However, it would not separate from the hydrocarbons upon cooling, apparently because of the highly viscous nature of molten ZnCl_2 , making a regeneration step difficult and expensive.

In this research project it was found that a mixture of $\text{KCl}:\text{ZnCl}_2$ in a 1:1 mole ratio, which is much less viscous than molten ZnCl_2 alone, would separate from the hydrocarbon phase upon cooling. Conversions in the range of 90% were achieved with this mixture at operating conditions of 4000 psi and 450°C . At lower pressures, in the order of 2500 psi, conversions of about 80% were still obtainable. Run durations of about one hour were found to be necessary in order to attain good conversions. It was also found that one batch of catalyst begins to lose its catalytic activity rather rapidly after it has been used for three runs.

The oil produced in the batch runs that were made contained a substantial amount of heavy material. An analysis of a combined sample of the liquid products showed that 50% of the product had boiling points above 600°F . Also, under the conditions studied, a high percentage of the MAF coal was converted to gas. Gas conversion ran in the range of 10% to 22% of MAF coal.

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COAL HYDROGENATION STUDIES
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JOHN SEBASTIAN MALSAM

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fulfillment of the requirements for the degree

of

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ABSTRACT

Previous research by Consolidation Coal Company had shown that zinc chloride was a superior catalyst for the hydrogenation of coal and coal extract. It gave rapid conversion to predominantly gasoline range liquids at low temperatures and pressure. However, it would not separate from the hydrocarbons upon cooling, apparently because of the highly viscous nature of molten ZnCl_2 , making a regeneration step difficult and expensive.

In this research project it was found that a mixture of $\text{KCl}:\text{ZnCl}_2$ in a 1:1 mole ratio, which is much less viscous than molten ZnCl_2 alone, would separate from the hydrocarbon phase upon cooling. Conversions in the range of 90% were achieved with this mixture at operating conditions of 4000 psi and 450°C. At lower pressures, in the order of 2500 psi, conversions of about 80% were still obtainable. Run durations of about one hour were found to be necessary in order to attain good conversions. It was also found that one batch of catalyst begins to lose its catalytic activity rather rapidly after it has been used for three runs.

The oil produced in the batch runs that were made contained a substantial amount of heavy material. An analysis of a combined sample of the liquid products showed that 50% of the product had boiling points above 600°F. Also, under the conditions studied, a high percentage of the MAF coal was converted to gas. Gas conversion ran in the range of 10% to 22% of MAF coal.

I. INTRODUCTION

Although the technology needed to hydrogenate coal to liquid products has been available since World War II, no process has been developed to this date which is economically feasible. There are many reasons why this is the case, including the cost of high pressure equipment, high catalyst costs, and the cost of hydrogen. Thus the hydrogenation of coal has become a subject for wide and varied research (1).

The reason why there is such a great amount of interest in the hydrogenation of coal is that the rising demand for petroleum products coupled with the falling reserve-to-production ratio of crude oil have made coal a prime candidate to supply much of the needed crude oil of the future. This is particularly true in the United States where the importation of foreign crude oil is restricted in order to keep this country from becoming dependent upon foreign sources for our energy requirements. Consequently, demand and advancing technology indicates that certain grades of coal will become economical sources of liquid fuels during the mid-1970's. (2)

Eastern Montana and the states adjacent to it are a vast source of coal. The Fort Union coal formation located in this area is estimated to contain 700 billion tons of coal. At the present rate of consumption this field alone could yield enough liquid fuels

to supply the United States for over 300 years. (3) Also, much of this coal can be strip mined and thus can become a cheaper source of raw material than are coals that must be mined by other methods. Thus it is that the Chemical Engineering Department at Montana State University has been active for many years in the study of coal hydrogenation using Montana coal as the raw material.

The study of the molten ZnCl_2 - KCl combination which is described in this thesis was undertaken with the objective of finding a cheap catalyst material. If such a cheap catalyst material could be found it would greatly improve the economics of coal hydrogenation.

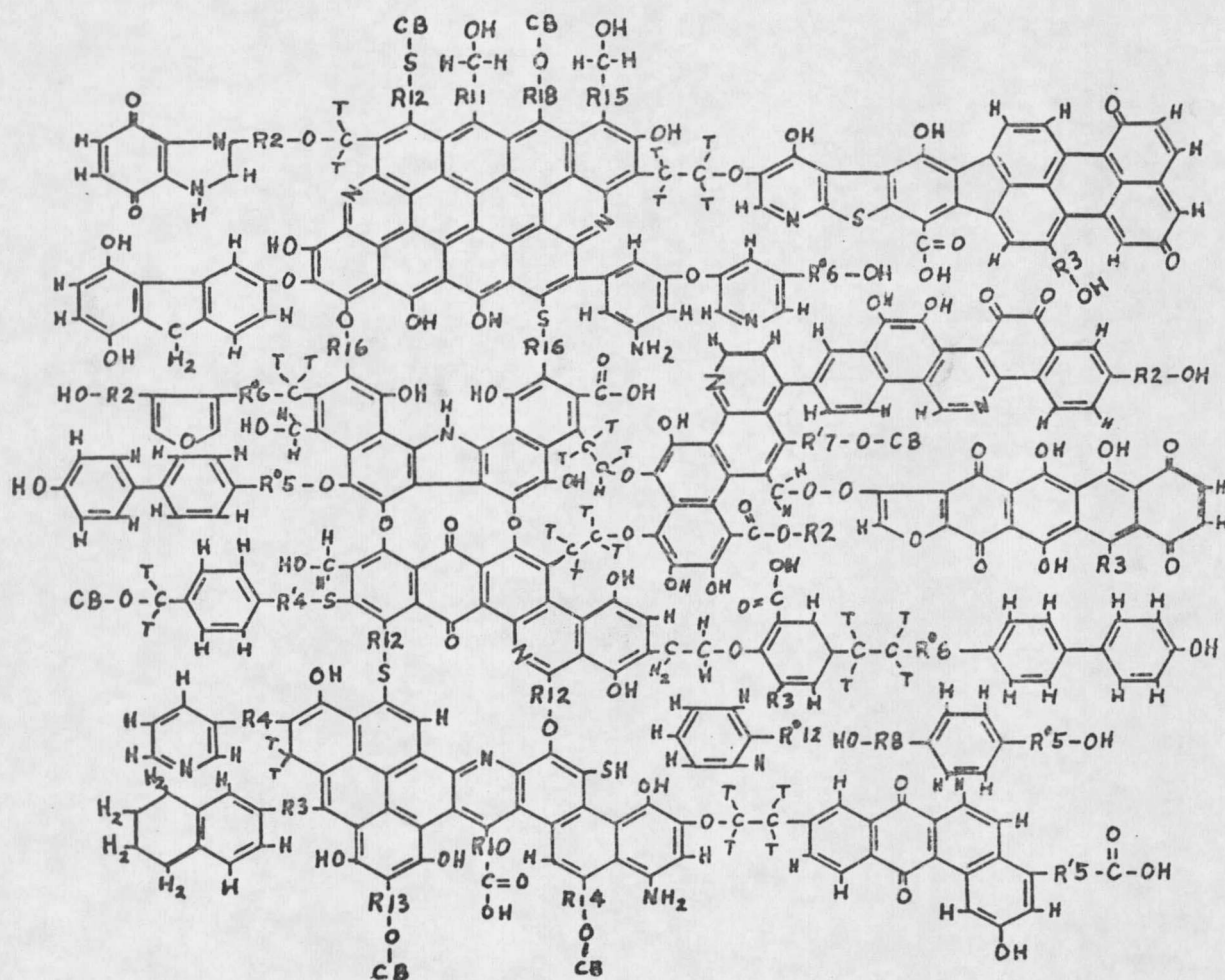
A. Coal Hydrogenation Studies using Molten ZnCl_2 Salt

The Consolidation Coal Company (working under the Office of Coal Research) has shown that the use of massive amounts of zinc chloride produces a superior hydrocracking catalyst for pyrene, coal, and coal extract. Their tests showed that molten ZnCl_2 , which is a Lewis acid, exhibited a high cracking activity and needed no additional catalysts to promote hydrogenation. They also found that zinc chloride is relatively inactive in the hydrocracking and hydrogenation of single-ring aromatics. (4,5,6) This is very significant because the structure of coal is highly aromatic, as shown in Figure 1.

The characteristics discussed in the previous paragraph make molten zinc chloride a superior catalyst to the commercial hydro-refining type catalysts. First, it gives a more rapid and complete conversion to gasoline-range naphtha products. The aromatic content in the products averages about 25 volume per cent and a high ratio of iso-paraffins to n-paraffins is produced. Thus it seems to be highly selective for the production of gasoline. Secondly, substantial conversions can be achieved at low pressures (of the order of 2000 pounds) and low temperatures (of the order of 350°C). (4,5,6)

B. Significance of Separating the Salt and Hydrocarbon Phases

The major drawback in the use of zinc chloride as a catalyst is that the nitrogen and the sulfur in the coal react with the salt and poison its activity. (7) Hence, if massive amounts of zinc chloride are used a regenerative step is necessary. The regeneration step or cycle is complicated by the fact that there is no appreciable phase separation between the salt catalyst and the coal or coal extract phase. Thus an extraction with water and an organic solvent is necessary in order to separate the spent salt from the products and unreacted coal. Then this water must be removed before the salt can be regenerated and returned to the system. This obviously increases the costs because of heat required for water



R°N Alicyclic Rings of N Carbons

RN Alkyl Side Chains of N Carbons

R'N Unsaturated Alkyl Chains

CB Cross-bonding to Other Heterocyclic Groups

T Tetrahedral Bonds

Figure 1. Typical Cross-Bonded Structure for High Volatile Coal (3)

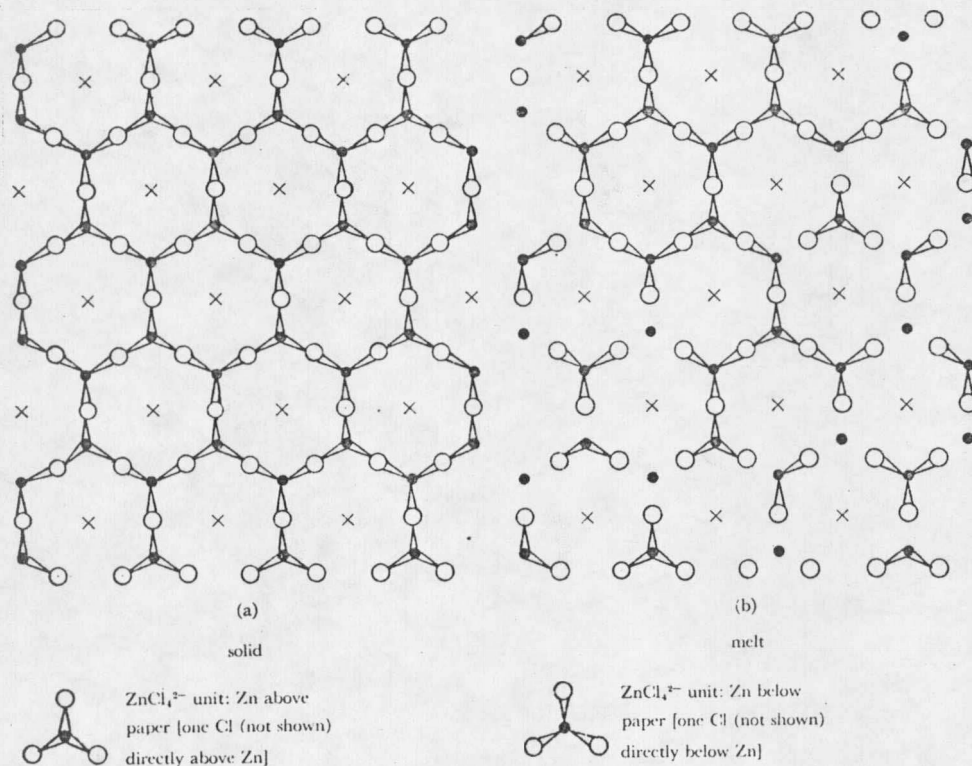
removal. Consequently, a catalyst which would separate from the coal phase would be much more amenable to a regeneration step. (7)

C. Studies of KCl-ZnCl₂ Salt Mixtures

A search of the literature on molten salts revealed that a mixture of potassium chloride and zinc chloride might yield the desired separation. A short sketch of the theory is as follows: (8)

The zinc halides form network structures in the molten state with very high viscosity and very low electrical conductance. Just above the melting point the proportion of free ions is very low. The postulated effect of melting zinc chloride is shown in Figure 2. Melting causes the network to break up as shown in section (b) of Figure 2. This shows the production of tetrahedral ZnCl_4^{-2} complex ions in equilibrium with larger sections of the network forming a viscous melt. It was felt that at higher temperatures progressive degradation of the network would first produce larger proportions of complex ions (which included ZnCl_3^- and ZnCl^+) and at still higher temperatures the simple ionic species Zn^{++} and 2Cl^- . (8)

There have been several investigations of pure zinc chloride systems using Raman spectroscopy. In molten ZnCl_2 there have been evidenced five bands which yield information regarding the state of molten ZnCl_2 . The effect of increasing the temperature is to in-

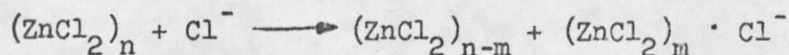


ZnCl_2 structure: (a) solid; (b) melt. Black circles represent Zn atoms (above or below plane of paper); open circles represent Cl atoms (in plane of paper). ZnCl_4^{2-} units are tetrahedral; the X's mark positions of Zn atoms (above or below plane of paper) belonging to neighboring layers.

Figure 2. Zinc Chloride Structure. (8)

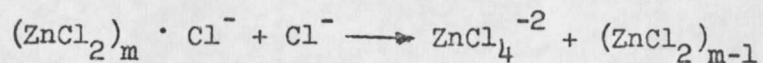
crease the intensity of a weak band at 305 cm^{-1} but increased temperature has no effect on those at 226 cm^{-1} and 250 cm^{-1} . These three bands have been assigned to the various vibrational modes of the $(\text{ZnCl}_2)_n$ polymer and the changes in the spectrum can be attributed to progressive depolymerization with increasing temperature. As was shown in Figure 2, the $(\text{ZnCl}_2)_n$ network or polymer is regarded as being composed of ZnCl_4 tetrahedra joined at the corners to give a three-dimensional array. Spectra showed that even at 500°C the vast majority of the Zn-Cl bonds are bridging rather than terminal. Hence, the network is still quite stable and therefore quite viscous several hundred degrees above the melting point. (8)

Further studies with Raman spectra showed that the spectra for ZnCl_2 is considerably changed if it is rich with KCl. The bridging Zn-Cl stretching frequencies of ZnCl_2 are reduced in intensity and the band at 250 cm^{-1} disappears on addition of KCl. There are also significant changes in the four other observed bands. All of these changes, however, can be explained by the depolymerization of the $(\text{ZnCl}_2)_n$ network on addition of KCl by the reaction



This process continues in steps upon further addition of KCl until a molar ratio $\text{ZnCl}_2:\text{KCl}$ of 4:1 is reached. On adding further KCl

the reaction



begins to predominate. R. H. Bloom predicted that the complete breakup of the $(\text{ZnCl}_2)_n$ polymeric network to form ZnCl_4^{-2} takes place at a $\text{KCl}:\text{ZnCl}_2$ molar ratio of 1:1. (8) Thus the mixture is much less viscous than a pure ZnCl_2 melt at the same temperature.

With this evidence in mind it was felt that a mixture of $\text{KCl}:\text{ZnCl}_2$ should form a much less viscous molten catalyst. It was hoped that viscosity might be the key to achieving phase separation while not significantly affecting catalyst activity.

II. RESEARCH OBJECTIVES

As can be seen from the previous discussion, molten ZnCl_2 seemed to have much promise as a coal hydrogenation catalyst except for the fact that it does not separate from the hydrocarbon products. In the light of this fact a research program was instituted with the following objectives:

1. To obtain a molten salt which would separate from the hydrocarbons upon cooling and still exhibit significant activity as a coal hydrogenation catalyst.
2. To examine how the conversion to benzene solubles using this catalyst varied with temperature, pressure, run length or contact time, and with the number of times the same catalyst material was used; i.e., catalyst life.
3. To make some elementary analyses on the gaseous and liquid products obtained using this catalyst.

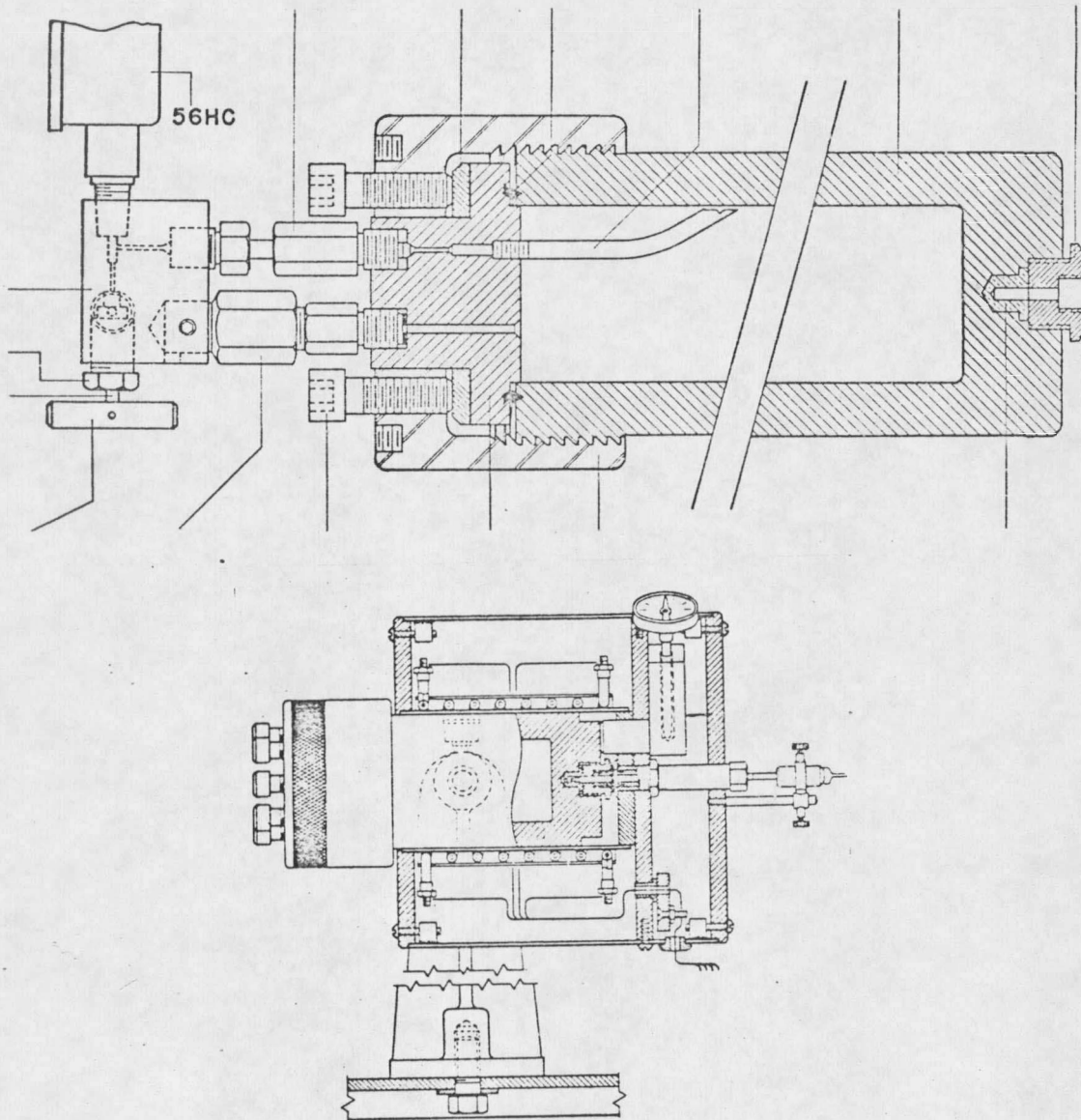
III. EXPERIMENTAL

A. Separation Studies

The first objective of the experimental work was to achieve phase separation. The apparatus used in this work was a 500 ml Parr stainless steel reaction bomb with an electric heater and a motor-driven oscillating mechanism. The apparatus is shown in Figure 3. The coal used in the experimental work was lignite coal from Savage, Montana, ground to less than 200 mesh. The KCl and ZnCl_2 were technical grade reagents purchased from the J. T. Baker Chemical Company.

In the initial series of runs the bomb was charged with KCl: ZnCl_2 salt mixtures in various mole ratios and anthracene oil. The bomb was charged to a low pressure (400 psig) of hydrogen and the mixture was contacted at 350°C for one hour. (The bomb was oscillating during the whole hour.) At the end of this hour the bomb was removed from the heater and allowed to cool in the air at room temperature. When the bomb was completely cool, the amount of free anthracene oil in the bomb was measured to determine the extent of the phase separation.

After this series was completed the same thing was done using coal and salt mixtures. Weight salt to weight coal ratios from 4:1 were used to determine how much salt was necessary to achieve good



Bomb Heater Details

Figure 3. Bomb and Heater. (10)

contact between the molten salt and the coal. These runs were also done at a much higher pressure (initial pressure 1900 psig) and at higher temperatures (400°C) to determine if the mixture showed any catalytic activity. After the bomb had been cooled, the pressure drop and the appearance of the hydrocarbon phase were used as evidence of reaction and, hence, catalytic activity. The bomb was then inverted and heated with a propane torch so that the whole reaction load fell out. It could then be broken open and examined for evidence of phase separation.

B. Conversion Studies

The next step in the research program was to determine the conversions that could be obtained using a 1:1 mole ratio of $KCl:ZnCl_2$ as the catalyst material. Before this could be done, an analytical procedure had to be devised. The one that was used is shown in Figure 4. In this procedure the gases were bled from the bomb into a gas holder. The bomb was then opened and the liquid products in the bomb were removed and filtered. The solids were removed and subjected to a twenty-four hour extraction.

The gases from the gas holder shown in Figure 4 were analyzed for light hydrocarbons on an Aerograph 90 gas chromatograph using a column of Poropak Q and hydrogen carrier gas. The chromatograph

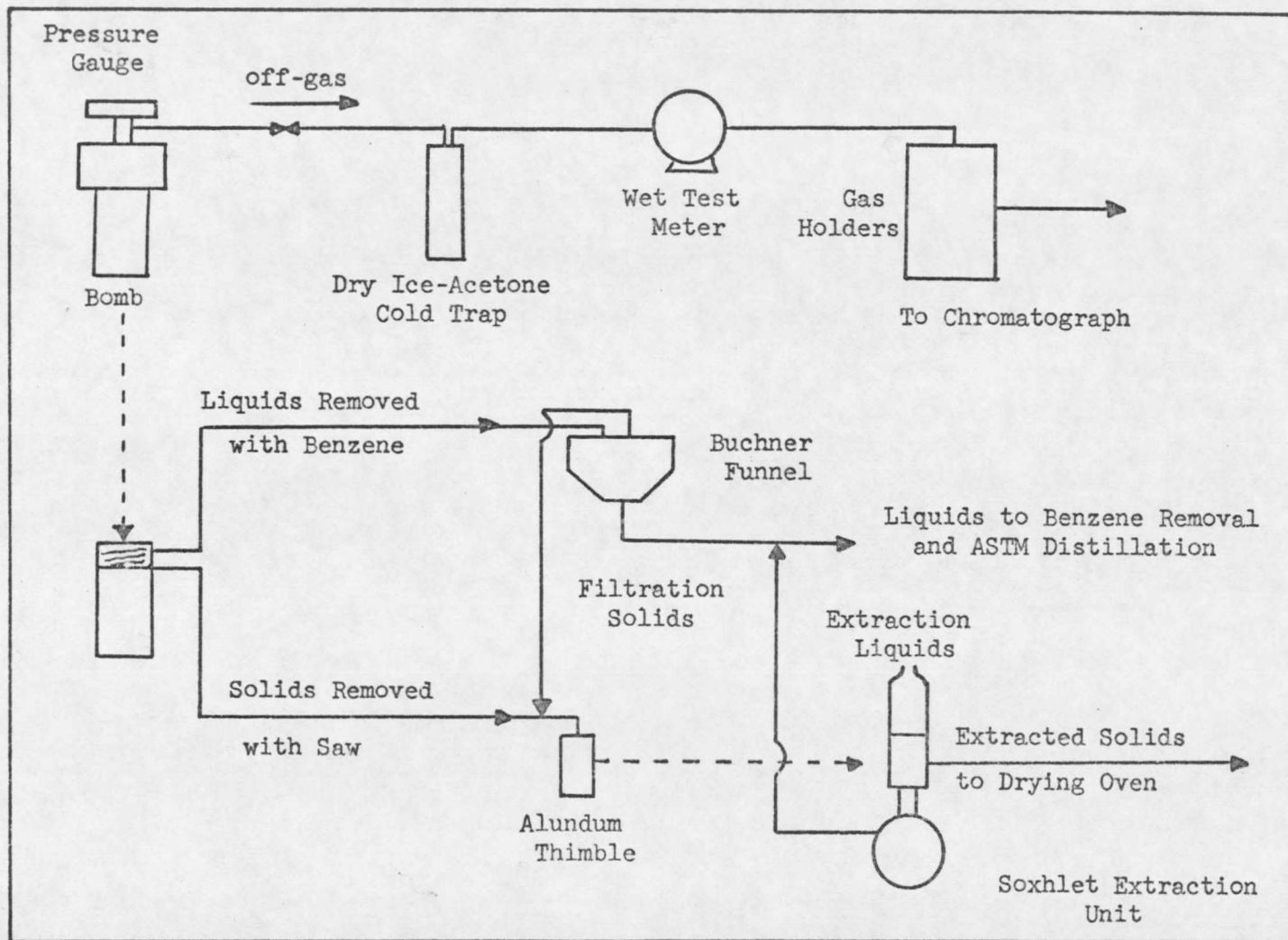


Figure 4. Product Analysis.

detected the light hydrocarbons (C_1-C_4) and CO_2 . The amount of H_2 in the off-gas was determined by subtracting out the mole per cents of the other constituents; i.e., by difference.

The liquids in the bomb and some of the light tars were removed from the bomb by washing it with benzene. This benzene solution was filtered and the solids combined with the other solids in the bomb. The benzene was distilled off of the product oil and the oil was subjected to an ASTM distillation. Since not enough oil could be obtained in each run, the oil from all the runs had to be combined. Thus the analysis is average oil product.

The solids in the bomb were removed with a circular saw. Both the hydrocarbon phase and the salt phase (mildly ground with a mortar and pestle) plus the solids from the filter were placed in a Soxhlet extraction unit and washed with benzene for 24 hours. After this the amount of coal converted to benzene soluble products was determined by the weight lost. The liquid from the Soxhlet was combined with the wash liquid.

Initially a series of runs were made to determine the reproducibility of the conversions and the limits of accuracy obtained with the analysis system. It was found that in order to get good reproducibility an alundum thimble had to be used in the extraction unit. Conventional cellulose thimbles were attacked by the $ZnCl_2$

salt if any water got into the salt. Also, the salt alone was put through the extraction to determine how much was lost in the process. After this initial series only one run was used to determine each experimental point because of the long amount of time and expense necessary for each point. In all of these runs and all of the following runs, 20g of coal and 80g of salt were used because separation studies had shown this would assure good contact between the phases.

The first variable that was studied in relation to conversion was reaction temperature. One-hour runs at 4000 psig operating pressure were made at 380°C, 435°C, 450°C, and 475°C. The next variable that was studied was pressure. One-hour runs at a temperature of 450°C were made at operating pressures of 1900 psig, 2750 psig, 3000 psig, and 4000 psig. After this the reaction time was studied. Runs of 10 minutes, 30 minutes, one hour, and two hours were made at 450°C and 4000 psig. A two-hour run was also made in which the bomb was cooled after one hour of operation and the gas was bled off. The bomb was then repressurized with fresh hydrogen and the second hour of the run was completed. This was done to see if it was hydrogen partial pressure or total run time which determined the limits of conversion. The final variable that was studied was the length of service of the catalyst. Five runs at 450°C and 4000 psig

-16-

were made with the same molten salt catalyst. The results of all of these runs were correlated with conversion.

IV. RESULTS AND DISCUSSION

The major objective of the research project was to develop a molten salt catalyst which would exhibit catalytic activity similar to ZnCl_2 and yet separate from the hydrocarbon phase upon cooling. It was found that a mixture of potassium chloride and zinc chloride in a mole ratio of 1:1 yielded the desired separation and catalytic activity.

Batch studies in a 500-ml reaction bomb indicated the trends that the conversion to benzene solubles followed with varying temperature, pressure, reaction time, and catalyst life. An analysis of the off-gas from the bomb allowed the calculation of the amount of charged coal converted to gaseous products. And finally, an ASTM distillation of the liquid products yielded a measure of the extent of hydrogenation of the liquids.

A. Separation Studies

In the initial stages of the research program the idea was to change some physical property of the molten salt to see if a particular physical property could be correlated to the tendency of phase separation. A search of the literature (in particular the book "Molten Salts" by R. H. Bloom) revealed that molten ZnCl_2 was still rather closely bonded and hence quite viscous. However, as previously indicated, Raman spectra studies showed the viscosity of the mixture

could be decreased very significantly by the addition of KCl. They further predicted that the molten ZnCl_2 complex would completely break down upon reaching a $\text{KCl}:\text{ZnCl}_2$ mole ratio of 1:1. (8)

To see if viscosity was the key to phase separation a series of runs were made using 150 ml anthracene oil (a coal oil) and an equivalent weight of various salt mixtures. These were brought up to mild conditions of temperature and pressure (to prevent significant hydrocracking of the oil) and contacted for one hour. It was found that decreasing the viscosity did increase the separation ability and that at a 1:1 mole ratio of $\text{KCl}:\text{ZnCl}_2$ essentially complete phase separation was achieved.

TABLE I: RESULTS OF A-SERIES

Am't of anthracene oil charged to bomb = 150 ml
Wt. oil = 171.4 g
Wt. salt added in all cases = 171.4 g
Initial hydrogen pressure = 400 psig
Operating temperature = 350°C

Run	$\text{KCl}:\text{ZnCl}_2$	Am't Oil Recovered	Final P
A-1	1:1	148 ml	100 psi
A-2	0:1	20 ml	80 psi
A-3	1:2	130 ml	100 psi

Having achieved successful phase separation with anthracene oil, the next step was to determine if the same separation could be achieved with a reacted coal charge. Since all the hydrocarbon reaction products were not oils as in the previous case, one could not just measure the separated oil. So the bomb was heated until the whole reaction load slipped out. This undoubtedly carbonized some of the oily products but allowed the whole charge to be broken open and examined for evidence of phase separation. One of the charges examined in this manner is shown in Figure 5. It was found that a 1:1 KCl-ZnCl₂ mixture again yielded essentially complete phase separation. Conversely, a test run with ZnCl₂ alone showed no evidence at all of phase separation.

Along with the separation studies, the examination of the charges allowed a determination of how well the molten salt had contacted the coal. This was done by noting the relative size of the separated layers. It was found that at equal weights of coal and salt some of the coal never came in contact with the salt at all. At a salt-to-coal weight ratio of 2:1 all of the coal came in contact with salt but the salt layer was small compared with the hydrocarbon layer. Consolidation Coal Company's work with ZnCl₂ had shown that a weight ratio of salt to coal of 3 was necessary for good contact and conversion. (8) To gain approximately the same amount of ZnCl₂



Figure 5. Phase Separation

in the molten state it was determined that a salt mixture to coal weight ratio of 4:1 would be used. An examination of a run with such a charge showed good contact between the coal and salt mixture.

A final factor that had to be determined in this series of runs was whether the 1:1 mixture of $KCl:ZnCl_2$ exhibited catalytic properties. For this reason the runs were made at much higher pressures and temperatures than the oil runs. All of the runs exhibited about a 200 psig pressure drop when they were cooled, indicating that hydrogen had been absorbed. Also, the hydrocarbon phase was a tarry mixture indicating that the coal had indeed been hydrogenated. Thus the next step in the research program was to determine the limits and conditions of conversion.

B. Conversion Trends

The first step in the conversion analysis was to make a series of identical runs to determine the reliability of the analysis procedure. The first series met with failure as considerable scatter occurred. This scatter was found to be due to the fact that cellulose thimbles were being used in the Soxhlet extraction unit. When these thimbles had been run for 24 hours, tiny pin holes appeared in them, which had allowed some solids to escape. It was found that $ZnCl_2$ which had gotten wet (either through absorbing reaction water

or getting water hygroscopically from the air) tended to attack the thimbles. To alleviate this problem it was necessary to use ceramic (alundum) thimbles in the units. With these alundum thimbles the conversions calculated at the same conditions varied only by $\pm 2.20\%$.

From this point on only one run was made for each data point. The reason for this was the time and expense involved in each run. Also, because in the next series of runs what was more important than the actual number were the trends that were observed. So with the knowledge that the analysis was accurated to about 2.5% the runs proceeded.

The first variable that was studied was the run temperature. Five runs were made at temperatures of 370°C to 475°C. It was found that at 370°C the salt did not separate completely from the coal and oil phase. At all other reaction temperatures essentially complete phase separation occurred. It was postulated that the reason for this was that the salt mixtures solidified sooner (due to lower temperatures) than at the higher temperatures, thus not allowing the salt time to settle to the bottom. Figure 6 is a cooling curve for the bomb from temperature of 450°C. The literature indicates that the melting point of a 1:1 mixture of $\text{KCl}:\text{ZnCl}_2$ should be near 228°C. (9) So at 370°C the salt has about five minutes less cooling time than at 400°C.

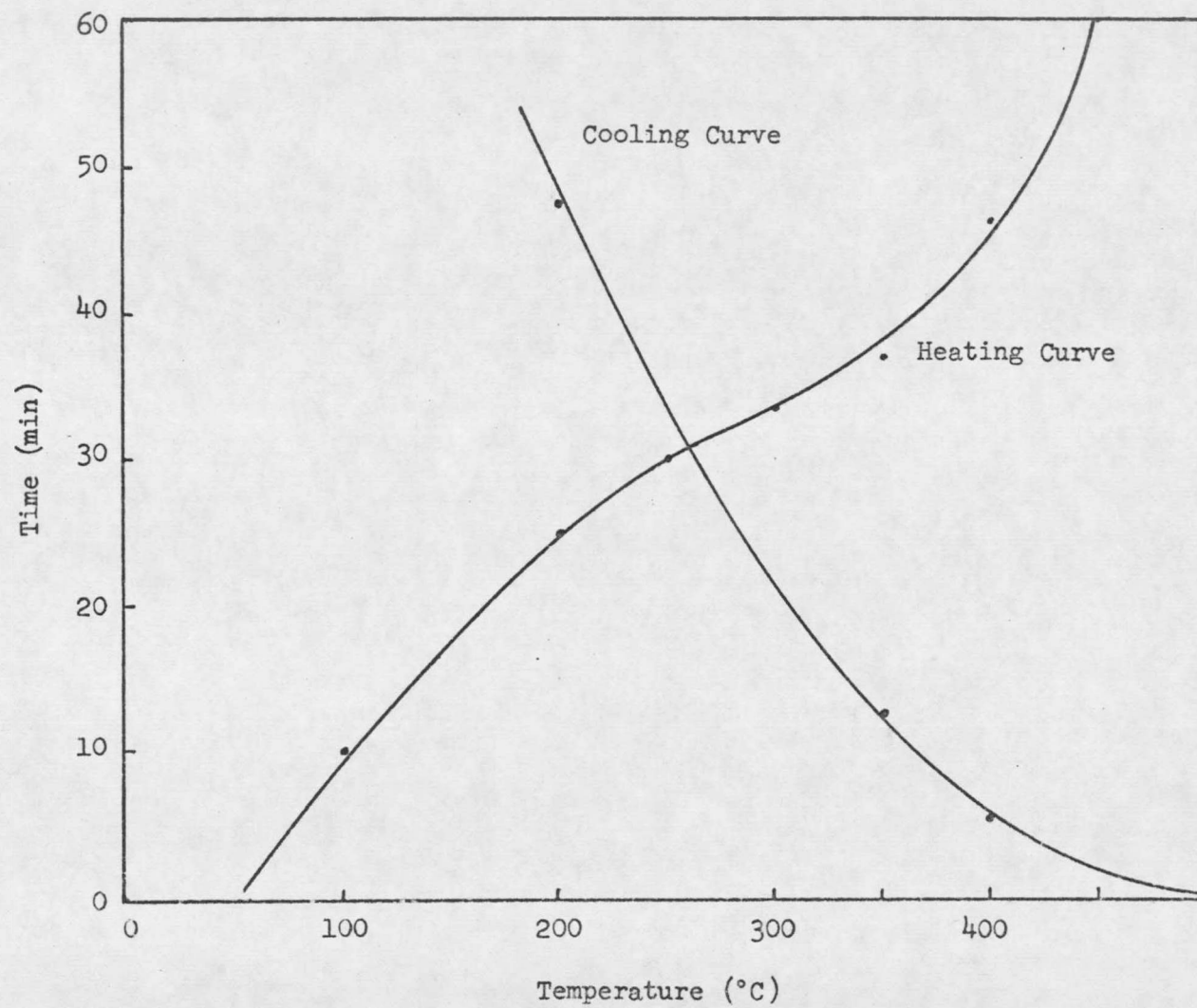


Figure 6. Cooling and Heating Curves at Operating Temperature = 450°C .

The conversions for the other four runs are plotted against temperature in Figure 7. It can be seen from this figure that at temperatures of 450°C and above conversions of about 90% and over are available. At temperatures below 400°C the conversion drops off rapidly. Also not shown on the graph is the quality of the product made. Visual examination of the reacted contents indicated that much more oil was produced at the higher temperatures.

After the temperature studies the next variable which was considered was the pressure. Figure 8 shows the results of the pressure studies. At high pressures, i.e., in the order of 4000 psig, conversions in the 90% range are possible. However, at milder operating conditions, i.e., in the order of 2500 psig, conversions in the 80% range are still available. Thus substantial conversions can be achieved without going to extremely high pressures.

The third variable which was examined was the run time or run length. Figure 9 represents the results of this examination. The study showed that a run time of about 60 minutes is necessary to obtain high conversions. Increasing the run length to two hours did not substantially increase the conversion but did yield essentially the same conversion as a two-hour run with one shot of hydrogen. However, not enough oil was produced in each run to see if there was a substantial difference in the oil products.

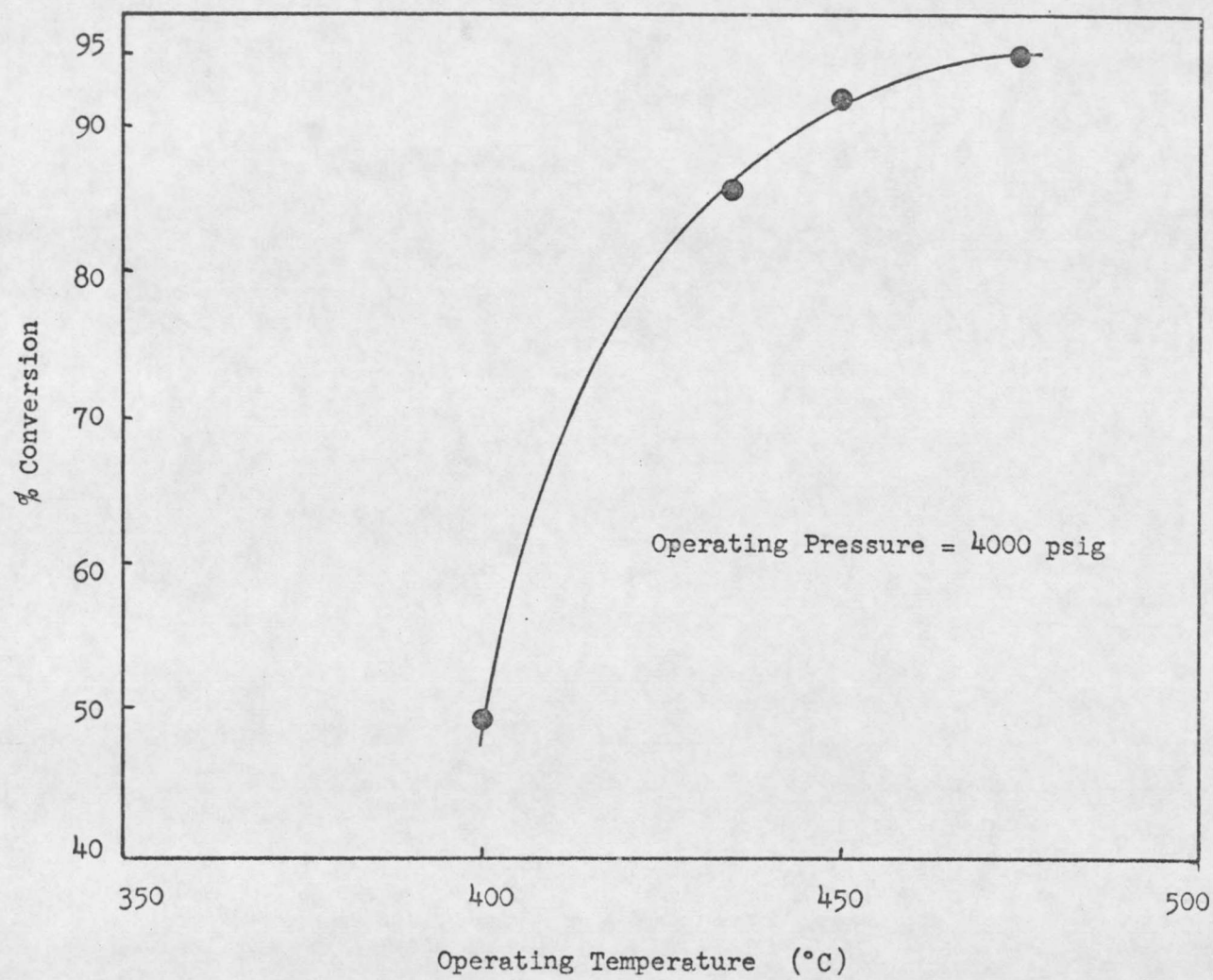


Figure 7. Conversion vs. Operating Temperature.

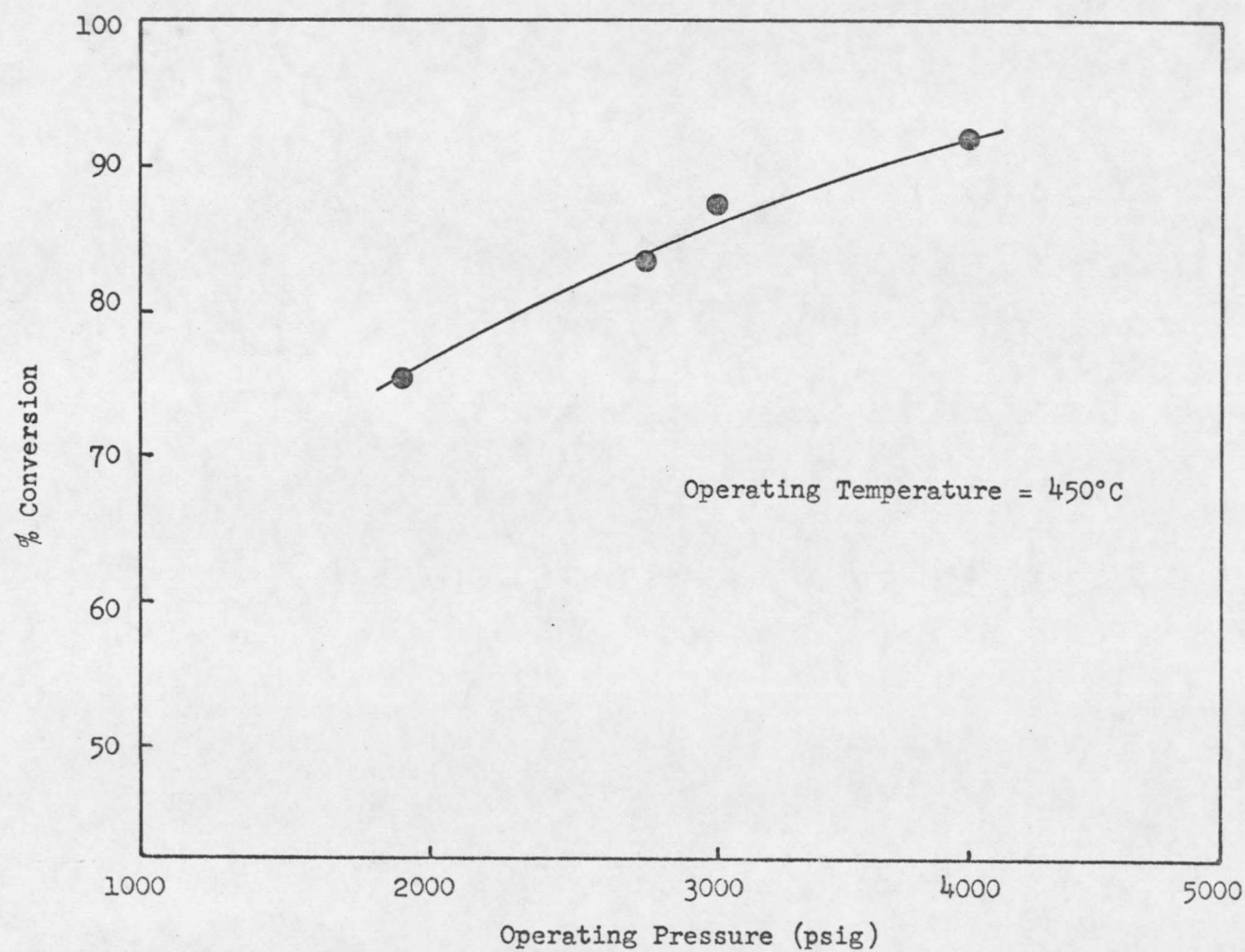


Figure 8. Conversion vs. Operating Pressure.

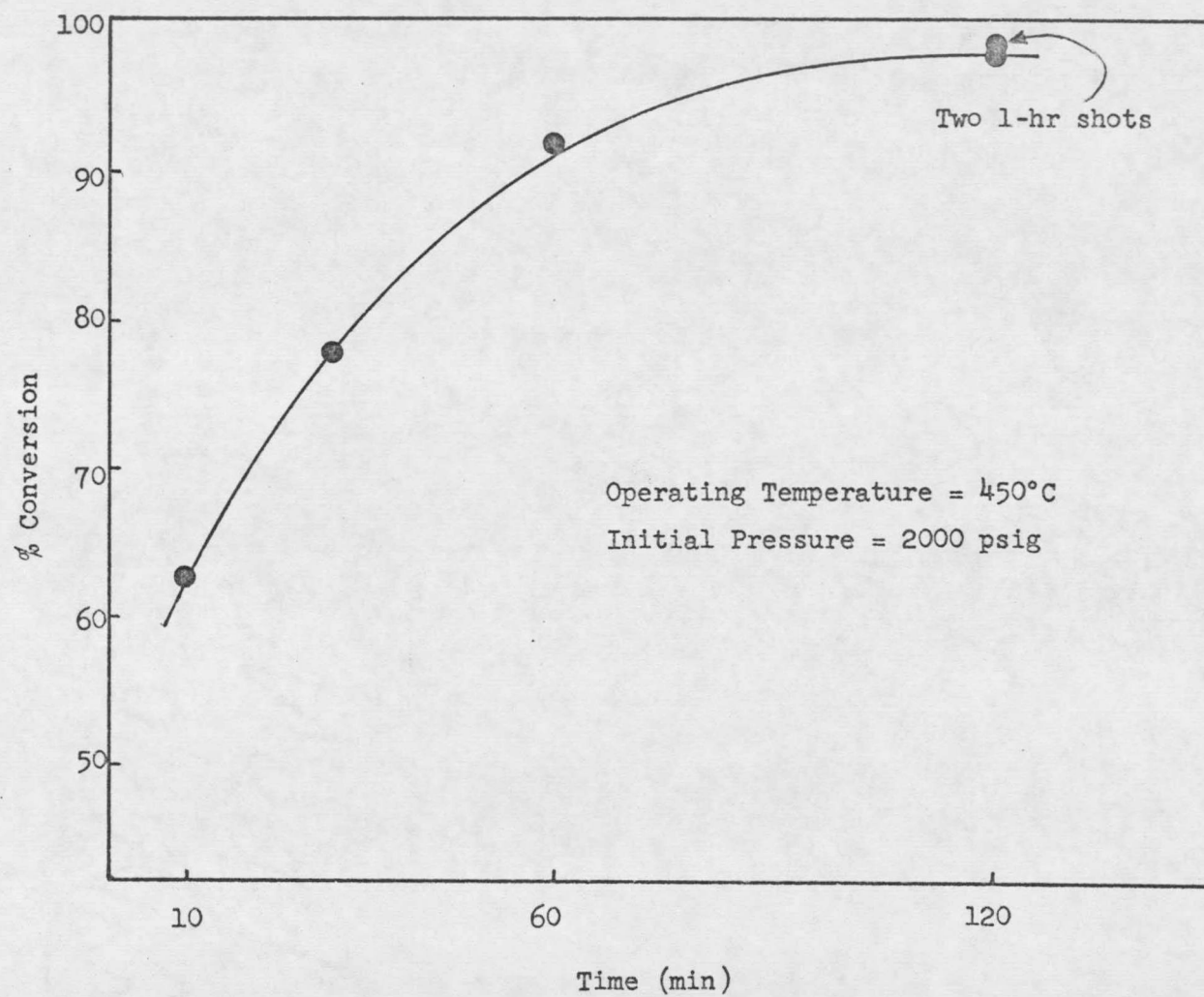


Figure 9. Conversion vs. Run Length.

The time scale does not indicate the total time the coal was in contact with molten catalyst. It only indicates the amount of time that the load was held at the reaction temperature of 450°C. As can be seen from Figure 6, about 33 minutes of heat-up time and 38 minutes of cooling time should be added to each run to get a total contact time with molten catalyst.

The final variable that was considered was catalyst life. To do this the same catalyst was used for five different runs of one hour at 450°C and a reaction pressure of 4000 psig. Figure 10 shows the result of this study. After five runs the catalyst activity has been severely retarded, apparently due to the sulfur, nitrogen, and ash in the coal. Also, as the salt was used over and over, less light liquid and more heavy tarry material was produced. This indicates strongly that a good salt regeneration system would be necessary in a continuous unit using the molten salt mixture.

C. Product and Gas Analysis

Because not enough oil was produced during each run it was not possible to construct a distillation curve for each run. However, it was possible to collect the oil from all the runs and make an average analysis. This was done with the results shown in Figure 11. As can be seen from the curve, only 50% of the product put

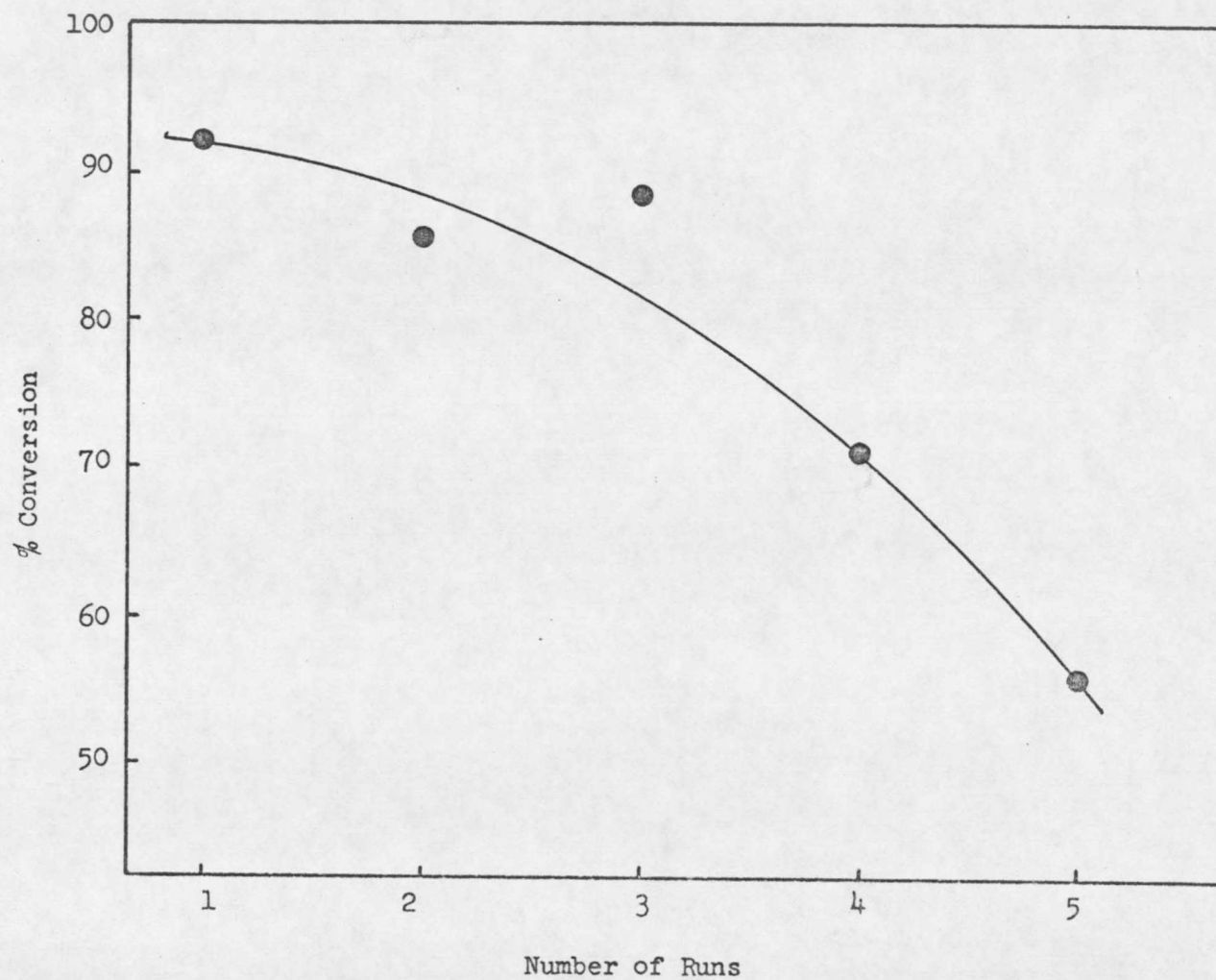


Figure 10. Conversion vs. Number of Runs with Same Salt.

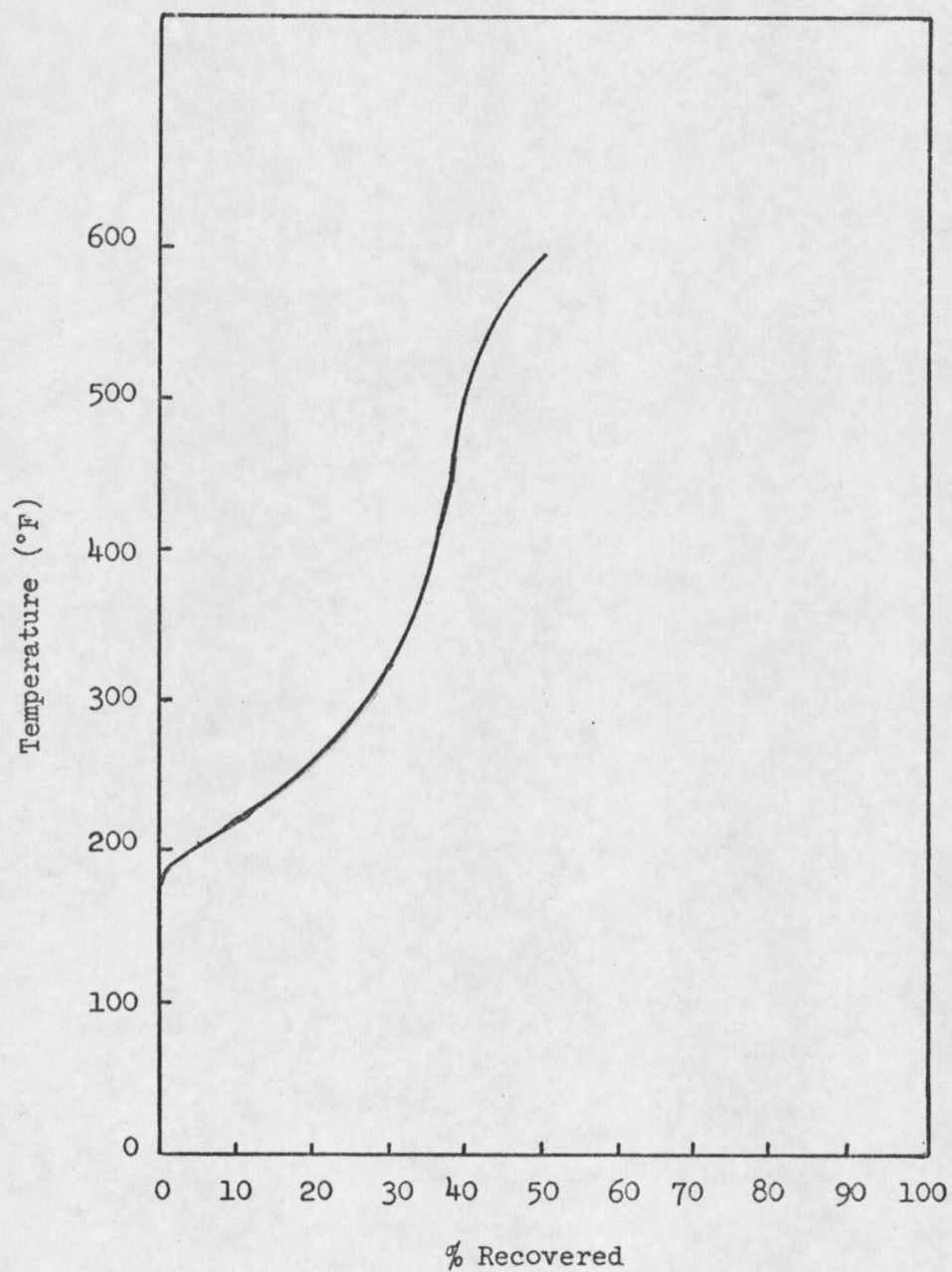


Figure 11. ASTM Distillation Curve
for Product Oil.

in the distillation flask was recovered. At 600°F decomposition of the materials remaining in the bomb was observed and the distillation was terminated. Thus, 50% of the reaction products are a heavy tarry material boiling above 600°F. If it had been possible, with the equipment available, to maintain a constant hydrogen partial pressure during the runs, it may have been possible to get more hydrogenated products. Also, it is hypothesized from the observations of the oil products that the runs at high temperatures and high pressures would show a higher liquid content (i.e., boiling below 600°F) than would the oil produced at milder conditions.

The gas analysis was made on a gas chromatograph using a Poropak Q column. Since hydrogen was used as the carrier gas, the column detected CH_4 , CO_2 , C_2H_6 , and C_3H_8 . The rest of the gas was assumed to be H_2 . A typical gas analysis (450°C, 4000 psig) is shown in Table II. It shows that a high percentage of the MAF coal is converted to gas under the conditions shown.

TABLE II. TYPICAL GAS ANALYSIS

Temperature = 450°C
 Pressure = 4000 psig
 Residence time = 60 minutes

<u>Yield Vol % Gas</u>	<u>Yield Wt % MAF Coal</u>
$\text{CH}_4 = 13.7\%$	$\text{CH}_4 = 16.6\%$
$\text{C}_2\text{H}_6 = 1.1\%$	$\text{C}_2\text{H}_6 = 0.62\%$
$\text{C}_3\text{H}_8 = 0.25\%$	$\text{C}_3\text{H}_8 = 0.97\%$
$\text{CO}_2 = \text{Trace}$	$\text{CO}_2 = \text{Trace}$

Remainder assumed H_2

Figure 12 shows how the yield of gas varies with reaction temperature. At 400°C it is only 10% of the MAF but increases to 22.6% at 475°C. Therefore, under the conditions tested, a substantial portion of the MAF is converted to gaseous rather than liquid products. These calculations were made by assuming that the coal contributed C_1H_1 to CH_4 , C_2H_2 to C_2H_6 , and C_3H_3 to C_3H_8 .

The variation in gas production with pressure is more difficult to describe graphically because as the pressure drops so does the conversion. Therefore, in reporting this variation the method used by Consolidation Coal Company was used whereby the weight percent of MAF coal converted to $\text{C}_1 - \text{C}_3$ gases is plotted against

conversion. (4) The results for runs of one hour duration at 450°C are shown in Figure 13. It shows that as the pressure is increased the gas production relative to the conversion attained increases. One would expect that this should reach a maximum and decrease as the pressure is increased further, but more experimental points were not available to confirm this hypothesis.

A thorough study of gas production and gas products at different temperatures and pressures would be necessary to determine the optimum run conditions. However, the elementary gas analysis shows that a high percentage of the MAF coal is converted to gaseous products under the conditions studied.

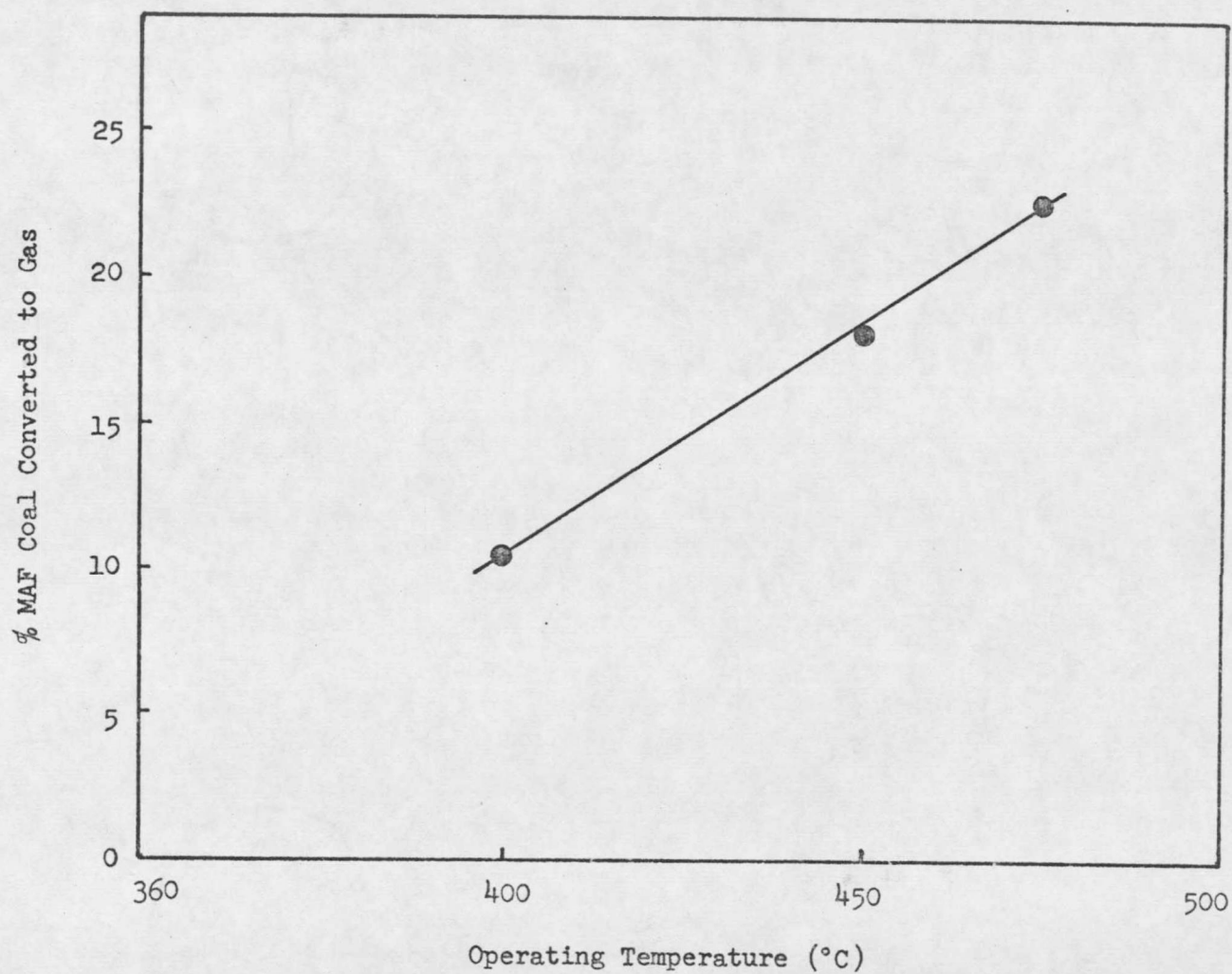


Figure 12. Conversion to Gases vs. Operating Temperature.

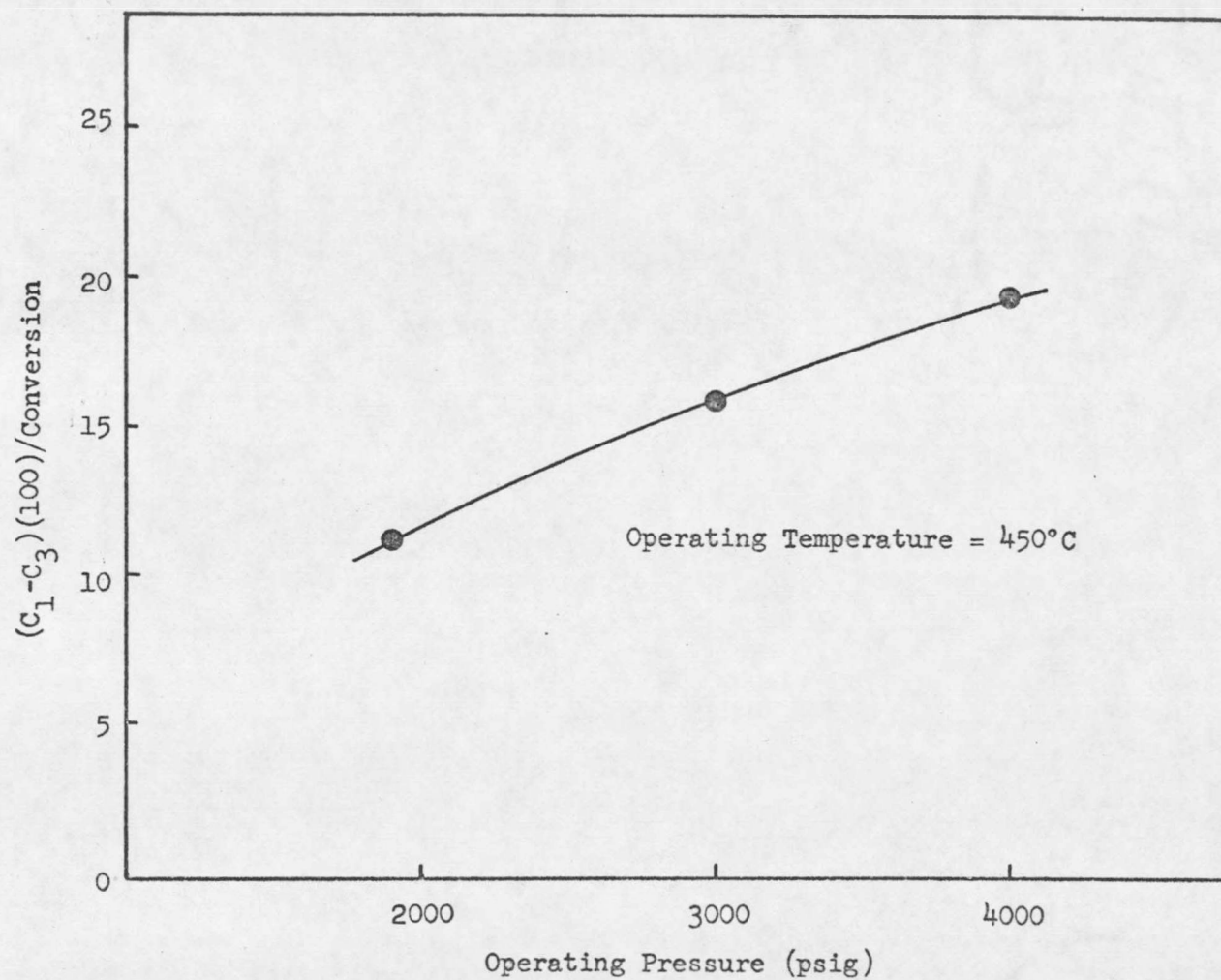


Figure 13. Gas Yield per Unit of Conversion vs. Operating Pressure.

V. CONCLUSIONS

1. Using a molten salt catalyst made up of a 1:1 mole ratio of $KCl:ZnCl_2$ will yield a coal hydrogenation catalyst which will separate from the hydrocarbon products upon cooling.
2. Conversions of 90% are possible at high temperatures ($450^{\circ}C$) and high pressures (4000 psi). However, conversions in the order of 80% are possible at much lower pressures (in the order of 2500 psi).
3. Run lengths in the order of 60 minutes are necessary to get good conversion.
4. The catalyst activity falls off rapidly after it has been used for three runs, indicating that a regeneration system would be necessary for such a catalyst.
5. The conversion products made in the batch hydrogenation studies contained a high percentage (approximately 50%) of tarry material boiling above $600^{\circ}F$.
6. Under the conditions studied, a high percentage of the coal (10% to 22%) was converted to gaseous rather than liquid products.

VI. RECOMMENDATIONS

1. Further research should be done with larger scale equipment so that enough product oil could be produced to measure the effect of the reaction variables upon the quality of liquid products produced.
2. Further research should be done on a continuous type of reaction unit to determine if separation could be maintained in the molten state for removal and regeneration of the salt.
3. Further research should be done on the salt which has been reacted to identify the impurities in the salt and find a way to remove them.

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VII. APPENDIX

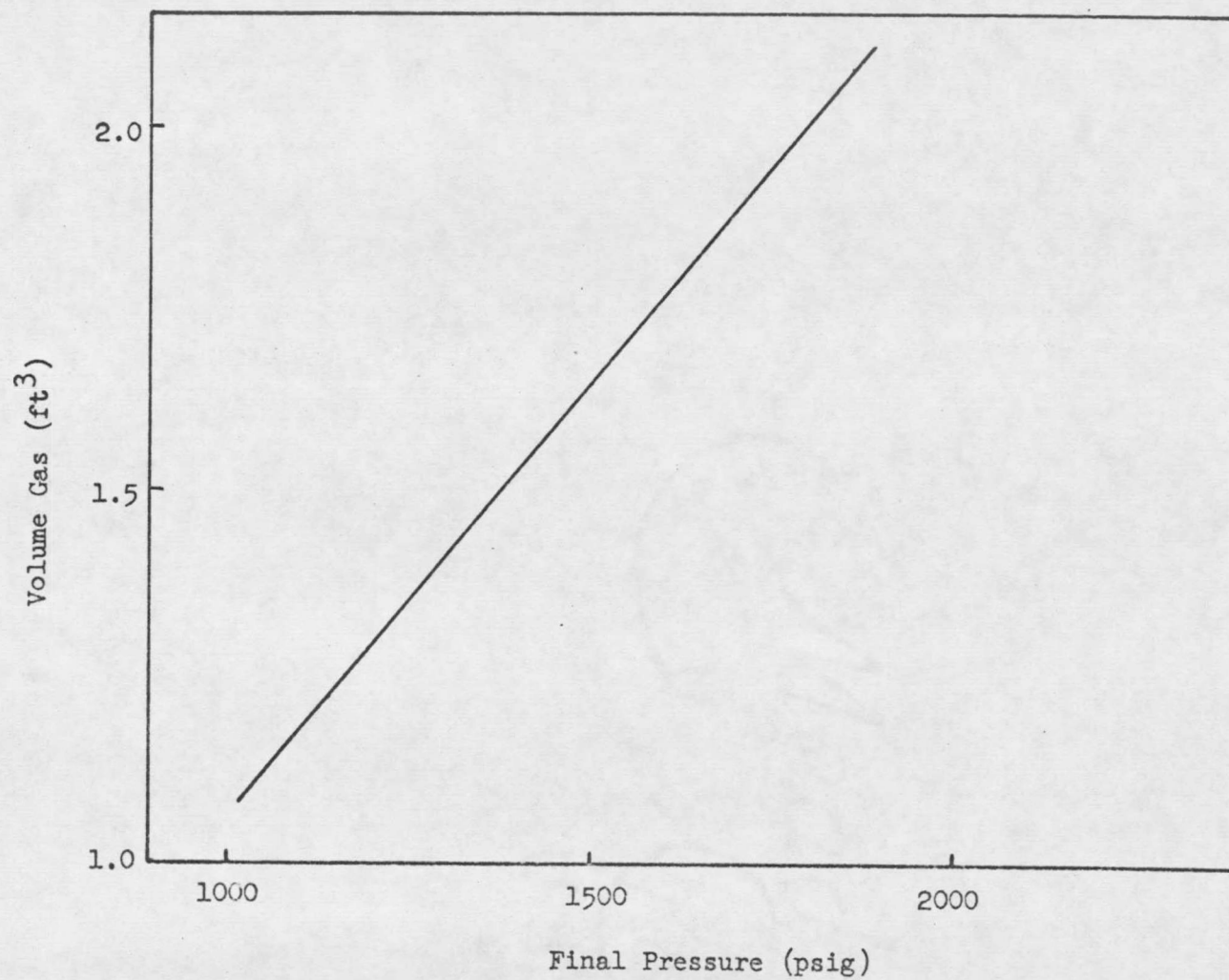


Figure 14. Volume of Gas in Bomb vs. Final Cold Pressure.

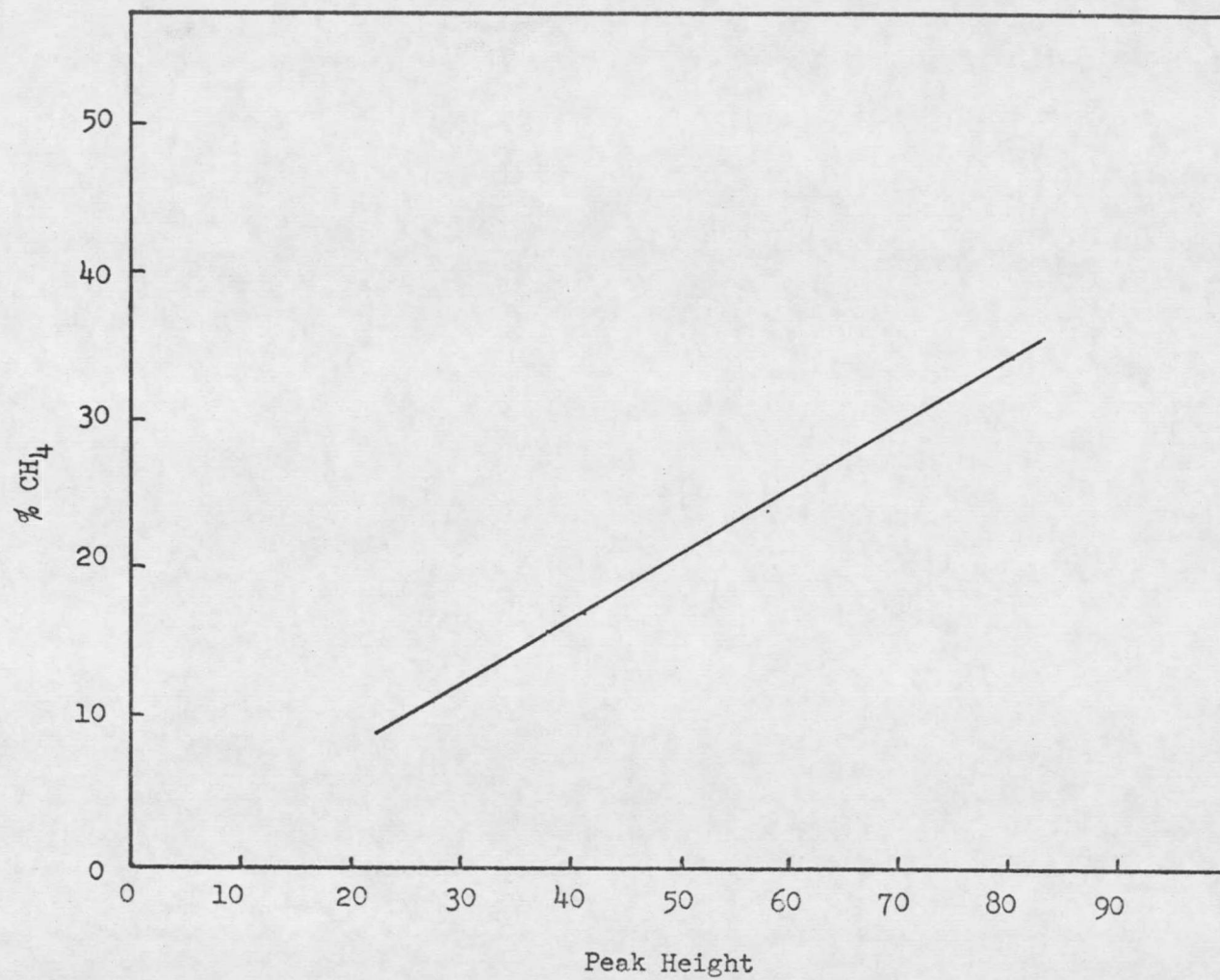


Figure 15. CH₄ Calibration Curve. Attenuation = 32.
(1-ml samples used)

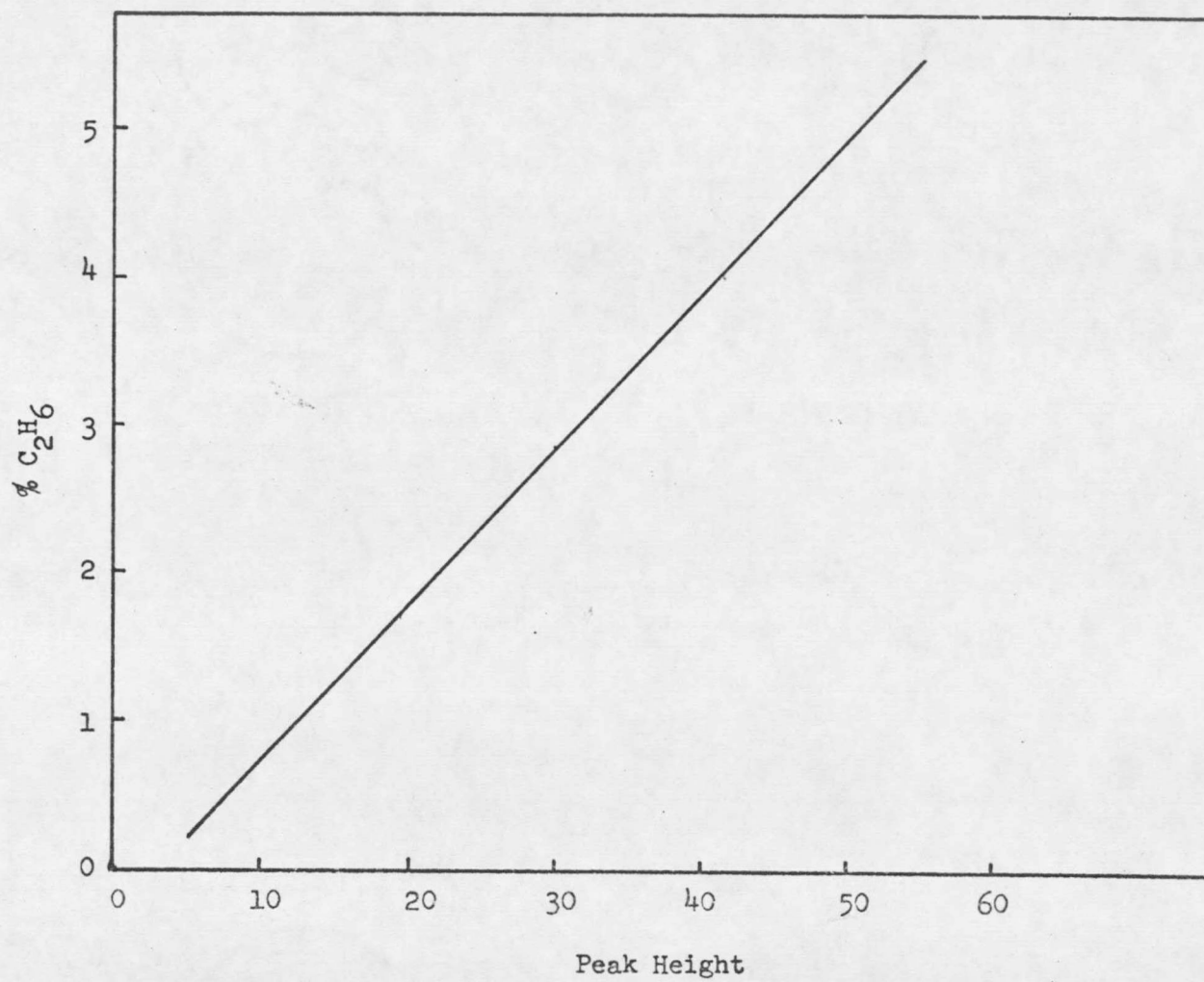


Figure 16. C_2H_6 Calibration Curve. Attenuation = 8.

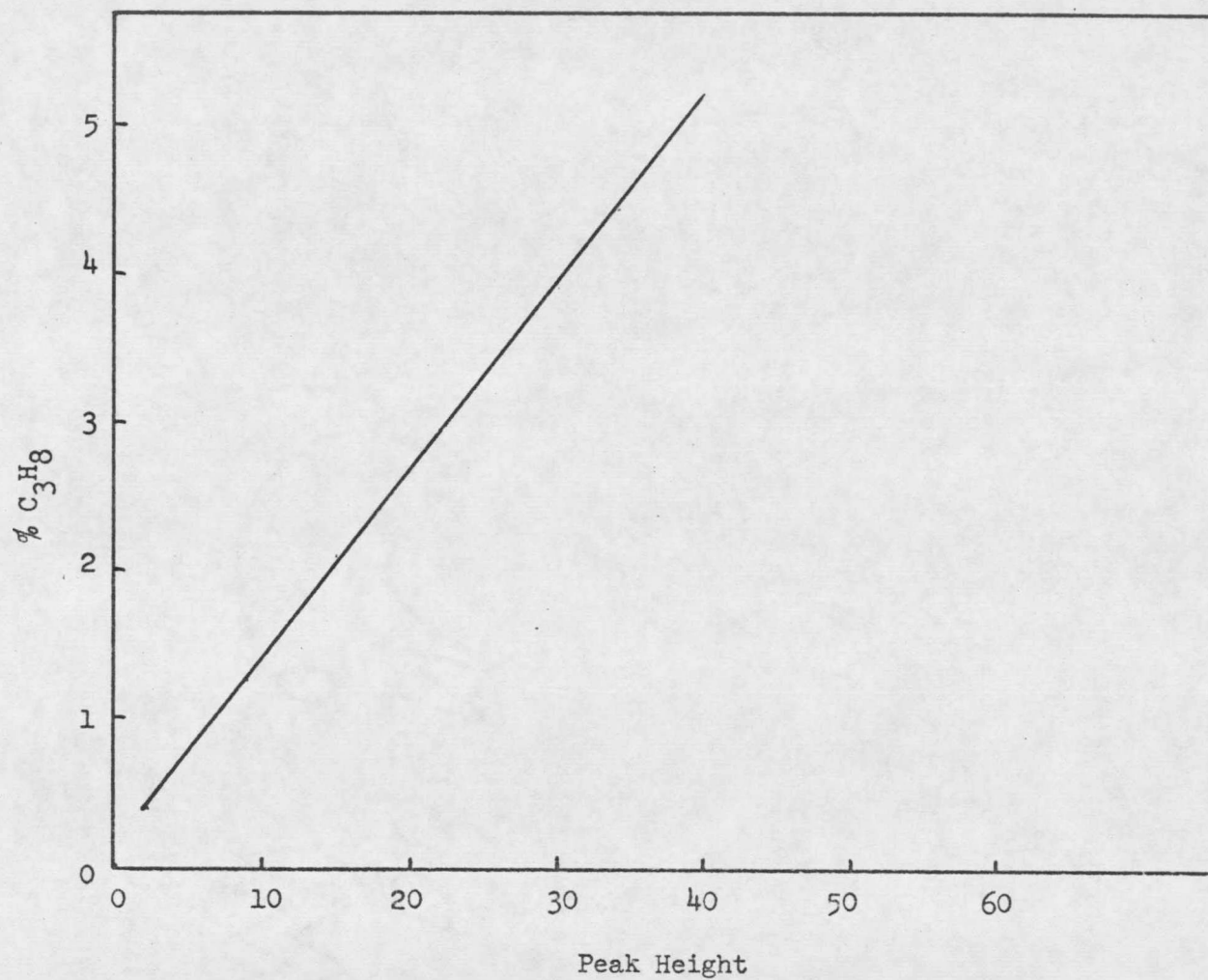


Figure 17. C_3H_8 Calibration Curve. Attenuation = 8.

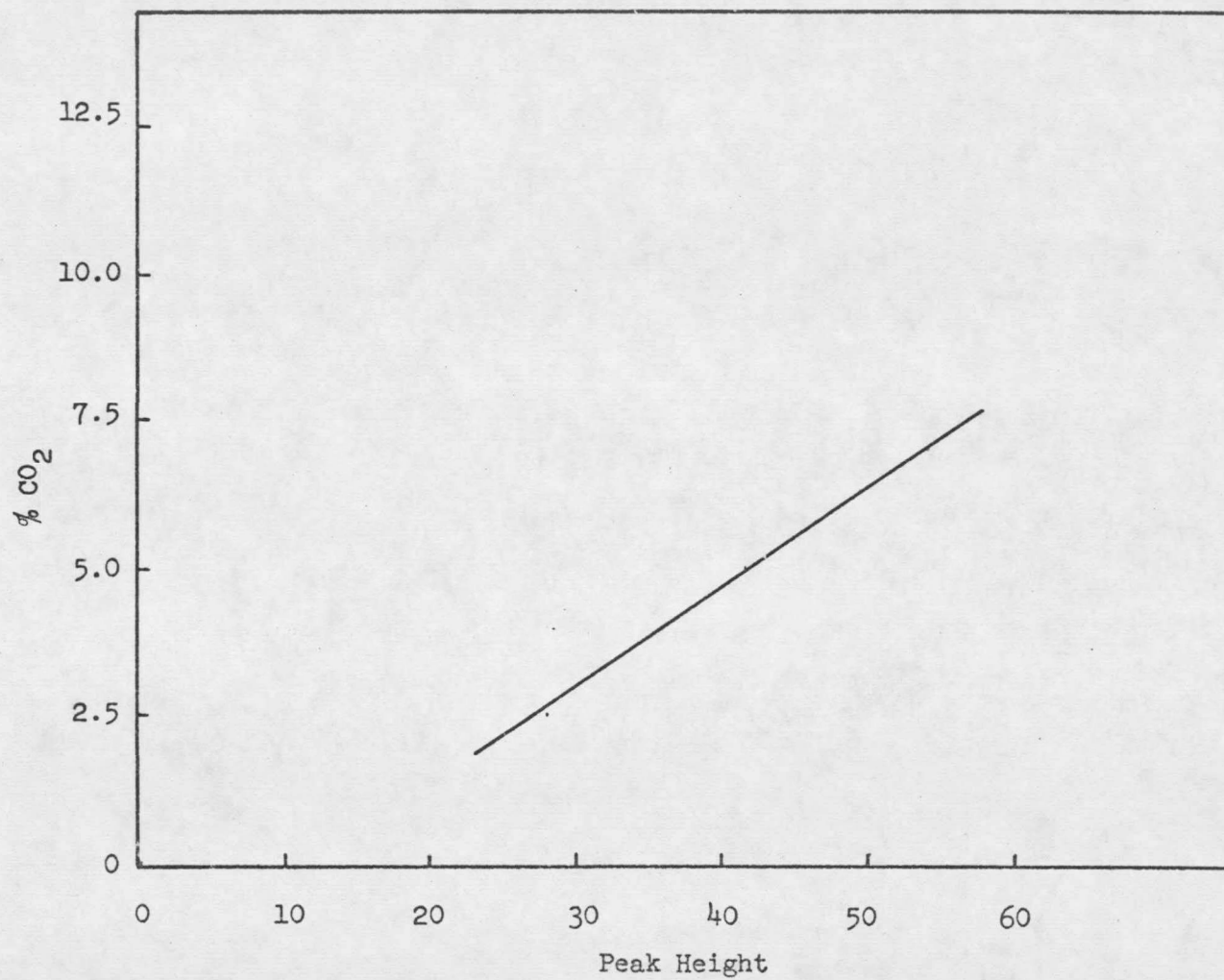


Figure 18. CO₂ Calibration Curve. Attenuation = 8.

CONVERSION CALCULATION

Final Wt Solids + Thimble + Beaker
- Wt Thimble + Beaker
Wt Solids
+ Wt Losses in Extraction
+ Bottoms Salts left in Bomb
Total Wt Solids
- Wt Salt Added
Wt V.M. + F.C. + Ash
- Wt Ash
Wt V.M. + F.C. Remaining

$$\% \text{ Remaining} = \frac{\text{Wt V.M. + F.C. Remaining}}{\text{Wt MAF Coal Charged}} \times 100$$

$$\% \text{ Conversion} = 100\% - \% \text{ Remaining}$$

Wt % MAF COAL CONVERTED TO GASES

$$\text{ft}^3 \text{ gas bled off} \times \frac{.938 \text{ mols}}{\text{ft}^3} = \text{mols gas}$$

Since vol % = mol %

$$\text{mols CH}_4 = (\text{mols gas})(\% \text{ CH}_4 \text{ in off-gas})$$

Exactly the same thing was done for C_2H_6 and C_3H_8

Assumptions

Coal contributed C_1H_1 to all CH_4 formed

Coal contributed C_2H_2 to all C_2H_6 formed

Coal contributed C_3H_3 to all C_3H_8 formed

Therefore:

$$\begin{aligned} \text{Wt coal converted to gas} &= (13)(\text{mols CH}_4) + (26)(\text{mols C}_2\text{H}_6) \\ &+ (39)(\text{mols C}_3\text{H}_8) \end{aligned}$$

$$\text{Wt \% MAF converted to gas} = \frac{\text{Wt coal converted to gas}}{\text{Wt MAF coal charged}}$$

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