1984

Pyrolysis and Gasification of Mississippi Lignite in a Fixed Bed Gasifier

J. E. Clemmer

C. W. Williford

Recommended Citation

Clemmer, J. E. and Williford, C. W., "Pyrolysis and Gasification of Mississippi Lignite in a Fixed Bed Gasifier" (1984). *Open-File Reports*. 76.
https://egrove.olemiss.edu/mmri_ofr/76

Open-File Report 84-7F

Pyrolysis and Gasification of Mississippi Lignite in a Fixed Bed Gasifier

J. E. Clemmer and C. W. Williford

1984

The Mississippi Mineral Resources Institute
University, Mississippi 38677

FINAL REPORT

SUBTASK C OF GRANT
" DEVELOPMENT OF MISSISSIPPI LIGNITES AND ZEOLITES "

MMRI-84-7F
(Bureau of Mines Grant# G1134128)

Pyrolysis and Gasification of Mississippi Lignite in a Fixed Bed Gasifier

Co-Principal Investigators

J.E. Clemmer
C.W. Williford

Department of Chemical Engineering
University of Mississippi
University, MS 38677

September 1984

TABLE OF CONTENTS

Page

Chapter

ABSTRACT

THE DEVOLATILIZATION OF MISSISSIPPI LIGNITE IN A LURGI GASIFIER

The sample of Mississippi lignite we used, contains about 40% volatiles, 20% fixed carbon, and 34% ash on a dry basis. The lignite has been pyrolyzed over a temperature range from 400 to 950 degrees Centigrade in order to observe the changes in volatiles released from the lignite in a lurgi type gasifier with a 325 mesh bottom screen and an inert atmosphere of helium. Material balance data has been gathered along with gas composition data from each experiment.

The data showed some scatter as was expected from the sample of lignite, but other variations of the data depended on the experimental apparatus. The amount of volatile remaining on the char decreased with increased temperature from 0.31 gram per gram dry-ash free (DAF) coal at 400 degrees Centigrade to 0.06 grams per gram DAF at 950 degrees Centigrade. The tar released can account for approximately 0.07 to 0.38 gram per gram DAF with no apparent pattern due to data scatter.

The gas produced increased from 0.08 to 0.25 grams per gram DAF over the range of increasing temperature with a corresponding decrease in the average gas molecular weight from 40 grams per gram mole to 17 grams per gram mole. This decrease in the gas molecular weight was caused by an increase in the production of hydrogen, carbon monoxide and methane while the total mass production of carbon dioxide per gram DAF remained approximately constant.

ACKNOWLEDGEMENTS

In addition to MMRI-84-7F, this work was supported by grants from the Mississippi Chemical Corporation and the Department of Chemical Engineering in the form of release time for the Principle Investigators, Ms. Amy Burrow who provided a great deal of clerical support and Mr. Art Bowles who helped us a great deal in construction and maintenance of the equipment.

Mr. Donald L. Farage, a graduate assistant, who was supported by the above grants, did the majority of the experimental work on this project and is substantially responsible for producing this document.

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Just under the surface of the gulf coast states lie deposits of twenty-two billion tons of lignite coal. Approximately twenty-five percent of this lies in the state of Mississippi (1). To a large extent the lignite coal has been undeveloped except for research sampling purposes. At least two lignite gasification projects are planned for Texas by Phillips Coal and Exxon, as well as TVA's plan for one in north Alabama. However, there are no active projects using the Mississippi deposit.

Large incentives exist to produce more local energy because of the high net import of energy. In 1980, the state imported $1.7 billion of various energy sources. The development of this resource would allow the state to increase its revenues from native energy (2).

The particular properties of lignite must be recognized in order to effectively use this resource. Lignite has a higher water content, 40% moisture as received, as compared to higher rank bituminous coals. The lignite is composed of 50% volatiles, 25% fixed carbon, and 25% ash on a dry basis (3). Three characteristics may prove significant for process selection. First, the coal is friable, with a large fraction reduced to dust during crushing. Second, the large potential volatile yield offers a range of liquid products and does so 100 to 200 degress Centigrade below bituminous and subbituminous coals. Third, lignite in general gasifies two to ten times faster than higher ranked coals.

The Lurgi Process appears inappropriate for use because crushing yields particles too small for fixed bed gasification. Other feasible methods are available for lignite gasification. These methods include the Koppers-Totzek opposing jets of entrained coal and the Texaco water slurry system. In all forms of gasification, coal, water, and oxygen are blended at high temperature to give partial combustion and drive the endothermic char gasification and water gas shift reactions.

A two stage system is used because of the high yield of volatiles from the Mississippi lignite. The first stage allows selective volatiliazation of marketable products. The second stage allows the gasification of the remaining char and unmarketable liquids into hydrogen and carbon monoxide.

Lignite devolatilization will probably yield such products as napthas, tars, and phenols. The char gasification will produce a hydrogen and carbon monoxide blend. Coal gasification's utility lies in it being economically favorable in comparision to other fuel options. Over $500 million in residual fuel was imported into Mississippi in 1980 (2). If an alternative could be found, then the state would benefit by allowing funds to remain in the state and thereby improving our economic status. Some residual fuels could be replaced by select liquid coal products. Combined cycle electrical generation could be an efficient use of the fuel gas (4). Also, the hydrogen and carbon monoxide mixture could serve as synthesis gas for the production of chemicals, such as ammonia for fertilizer as proposed by Brown (5).

The objective of this research was to determine the effect of final reactor temperature on volatile release and gas composition for Mississippi lignite coal.

CHAPTER II

LITERATURE SURVEY

The five billion tons of recoverable lignite are one of Mississippi's most undeveloped resources as stated by Luppens (1). The potential uses of this resource include: direct combustion, production low Btu fuel gas and aromatic chemicals by pyrolysis, production of fuel gas by steam gasification, and production of hydrogen for manufacturing ammonia by steam gasification.

There are several characteristics which are unique to Mississippi lignite and important in the linked processes of drying, pyrolysis (or devolatilization), and steam gasification. These include relatively high ash and moisture content which will effect any lignite utilization process. The proximate and ultimate analyses of Mississippi lignite as compared with other analyses can be found in Tables 1, 3 and 4 in Appendix A. Lignite is heterogeneous in nature as is reflected by the variance of the sulfur content from 0.5 to 5 percent as verified by ultimate analysis (6).

The following sections review stages of gasification and how coal properties, particularly for Mississippi lignite, affect gasification.

19____DRYING

Lignites have substantial water content of 40 to 60 grams per 100 grams of dry coal which affects practical reactor design in that drying of the coal must be considered (6,7). The moisture exists in four forms: bulk, capillary, physically, and chemically absorbed. The first three are removed during drying; the last about 0.04 gram/gram dry coal, during devolatilization. Three changes in the structure and characteristics of the lignite are caused by drying: vaporizing water suppresses particle temperature and devolatilization (2); solid restructuring occurs from water loss and thermal stresses (8); and very rapid heating (600+ degrees Centigrade per second) dries moist coal particles with less structural shrinkage and perhaps with pore enhancement from escaping steam (8). Mississippi lignites dried from 0.6 grams water per gram dry coal produces a 32 percent shrinkage (9).

Texas lignites can be crushed to give the quarter-inch nuggets required for use in the Lurgi gasifier. However, Mississippi lignite is more brittle and can be crushed by hand to a diameter of less than one millimeter. This factor and the previously mentioned structural breakdown and particle shrinkage reduce the particle size to a point making the fixed bed gasifier difficult to use in an industrial aplication. Fortunately, our experimental design adapts to handle the physical problems of the pulverized coal by using a small reactor screen and by using particles larger than 250 microns. industrial scale there are several reactor systems that can handle this type of coal. Among these are Koppers-Totzek opposing jet, Westinghouse fluidized bed, and Texas slurry methods (5). There are certain advantages in the use of pulverized coal. The coal particles heat up faster resulting in higher volatiles yield and also a higher yield of gas(10).

B) DEVOLATILIZATION

The exact chemical structure of coal is difficult to describe due to its immense complexity. We do know that the structure of coal includes aromatic rings joined by oxygen linkages in which carboxyl and carbonyl groups are present and heterocyclic rings with sulfur, nitrogen and oxygen. During devolatilization, after drying, the particle temperature rises rapidly to 200 to 300 degrees Centigrade. At this point in the particle's temperature history, the coal structure begins to decompose. Wen and Dutta (10) hypothesized a series of processes comprising decomposition which is shown in Table 25 in Appendix A.

The volatile products leave the coal surface and begin to diffuse through the porous structure of the particle to its exterior. Complex compounds like condensed ring aromatics can polymerize and deposit on the porous surfaces and then further decompose to coke. Some of the volatiles react with hydrogen, stabilize, and diffuse out of the particle. Anthony, Howard, Hottel, and Meissner (11) indicated that temperature apparently controls the rate of decomposition of the coal. However, a combination of four parameters determines product yield: (1) the ultimate temperature; (2) heating rate; (3) particle size; and (4) atmosphere in and around the particle. These factors influence the rate of diffusion as well as stabilization and escape of secondary products (11).

H_Ulțlniațe_IâQl£erațune

The ultimate temperature represents the final temperature achieved by the sample during an experiment. Volatile yields are affected by the ultimate temperature through the types of compound that are decomposed and the decomposition rates of each compound. The hypothesized order of reaction by Wen and Dutta (10) suggest that at an ultimate temperature of 500 degrees Centigrade the carboxyl and carbonyl groups would decompose. This temperature would not, however, have much effect on the carbon to hydrogen bonds. Therefore, the gas produced would be rich in carbon monoxide and carbon dioxide, but would not contain a large amount of hydrogen.

¿l_Hsaţjji£KâLe

The heating rate effects the yield and composition by forcing the volatiles out of the particle more rapidly. This reduces the residence time of the volatiles in the particle. Wen and Dutta (10) have shown that the yield of volatile matter increases by a factor of three as the heating rate increases from one degree Centigrade per second to one-million degrees Centigrade per second. The volatiles produced differ with temperature in that at 500 degrees Centigrade the product is mostly liquid; but at 900 degrees Centigrade mostly gas.

According to Walker at Penn State, coal devolailized in 0.3 seconds has a char gasification rate 17 times faster than a char devolatilized in five minutes (12). Walker's hypothesis is that rapid devolatilization causes native calcium to remain dispersed and catalytically active during devolatilization, but slow heating allows the calcium to agglomerate. To conclude our comments, some investigators feel that rapid heating rate is related to, but not responsible for, higher yield (13,14).

iL·M(nos^i^Í£_E££eç£s_on_I)£y.£lat£Iiz.a£lon

The atmosphere under which devolatilization occurs affects conversion and product distribution. Anthony, Howard, Hottel, and Meissner (11) showed that pyrolysis weight loss of a bituminous coal varied from 50 weight percent at 0.001 atmospheres pressure down to 37 weight percent at 100 atmospheres pressure. Also, Suuberg, Peters and Howard (15) have shown that increased pressure suppresses volatile release, but that hydrogen partial pressure increases volatile release. Higher pressure increases volatiles residence time in the particle and hence allowing deposition, but hydrogen stabilizes reactive volatiles and allows them to escape the particle. This will increase the weight loss to the particle. Pressure and atmospheric effects only appear important above about 600 to 700 degrees Centigrade for rapid heating. Deposition reactions become more significant above this temperature (16).

âl Particle Size Effects

As particle size increases, volatile residence time in the particle will increases. This will allow for more contact of the volatiles and the lignite pore surfaces, therefore more chance for deposition of volatiles back in the particle. The deposition of the volatiles will reduce the weight loss from the lignite. During rapid pyrolysis the weight loss decreased from over 60 percent at 0.1 millimeter to 48 percent at 0.9 millimeter particle size (16). Scaroni, Walker and Essenhigh (14) have shown that the size of the particle in the range from 0.04 millimeters to 0.2 millimeters has no effect on the yield. Most of our experiments used particle sizes in the range from 0.25 millimeters to 0.59 millimeters.

CHAPTER III

EXPERIMENTAL APPARATUS

The reactor and support analysis equipment used in the devolatilization experiments will be presented in three major sections: A) the devolatilization unit; B) the gas chromatograph, and C) the proximate analysis coal analyzer. All of this information will be given in as much detail as is practical and necessary. Appendix B contains all the supporting figures referred to in this and following chapters.

ål__DLV.QLATlLIZ.AIIQN_UäIL_GLN£RAL

A basic diagram of the unit has been provided in Figure 1 to aid in the respective location of each section. All tubing components are made of either 304 or 316 stainless steel if they are exposed to the reactor gases or tars. The Swagelok fittings and the tube sizes ranged from one inch for the reactor, one-eigth inch for product gas lines to one-sixteenth inch lines in the gas chromatograph. The only section of the system that does not have metal tubing is the portion of the gas network going from the sample system to the glass saturator bottles and on to the wet test meter (Figure 1). This section of tubing is very short and is TYGON plastic tubing.

Ll_£AS_AO_ÇQAL_X^EUÏ_SÏ£IEM _

The helium carrier gas for the unit is supplied in bottled form and is regulated once from the bottle for bulk flow to the system and the coal hopper. It is regulated again for accuarate flow control to a rotameter. The rotameter is used in line to check the rough flow rate of the purge gas through the reactor. The helium rate is fine-tuned by the use of the wet test meter and accurately measured before each run with as bubble tube.

The coal is measured and placed in the hopper on top of the reactor. The hopper can be purged of air and pressurized with helium for sample injection. The sample is held from the reactor by a one-half inch ball valve below the hopper.

Both the coal and the helium flow downward into the heated zone to the reactor through one-half inch tubing.

Cl_REâCIO£_A&D_FURNAC£_ȘYâIEM

The reactor, from the top, consists of a one-half inch tube that joins a Swagelok reducing union which brings the reactor to one inch tubing (Figure 1). Both ends of the 28" reactor tubes have identical reducing unions and are kept outside the heated zone to prevent gauling. The lower union has been bored to allow the one-half inch tube to enter the one inch tube. On the end of the one-half inch tube is placed a specially machined sleeve welded reducing union that has not been welded in place (Figure 1). A 325 mesh (0.0017" sieve eopening) stainless steel screen fits snuggly atop the one inch end of the welded union. By sliding the tubing up into the bottom union, the welded union and screen can be placed in the lower edge of the middle section of the furnace. With the screwed fittings outside the furnace we are allowed access to the screen and the reactor internals for examination. If these parts were inside the furnace then they would be hopelessly weled together after the first run.

The furnace is a three zone, 2000 watt Marshall model 20235 split furnace. It is mounted vertically on a rail car which allows for easy removal of the furnace at the end of a run. Each zone of the furnace has its own type K Love controller. This helps achieve even heating down the furnace.

The exit gas temperature is measured by a type K thermocouple stationed just below the reactor screen. This thermocouple is connected to a model 400 a trendicator temperature indicator.

D}_ŢAK_CQLLECIION_ŞiaiEM_

Both the hot tars and gas leave the bottom of the reactor through one-half inch tubeing and is reduced to one-quarter inch tubing before entering the first tar trap. The traps are constructed of a one inch cap fitting. The cap has a center tapped hole bored in it with a rounded one-quarter inch union silver soldered in place. To one side of the center, a one-eighth inch hole was bored and a section of the same size tubing was also silver soldered in the hole to allow the gases to leave. The center union has been center bored to allow the one-quarter inch tube from the reactor to pass down into' a 25mm x 100mm pyrex culture tube. The culture tube is sealed to the cap by a one inch nut and teflon ferrei set. Both traps are constructed in similar fashion and are placed in ice baths for an experiment. This successfully stops all tar and water from reaching the gas sampling system.

E)_SAMPLES_AND_VOLUME_MEASUREMENT_SYSTEM

The cleaned gas from the reactor and tar traps now must be sampled for composition and its volume measured. In Figure 1 the piping arrangement of the sample network equipped with a palladium hydrogen transfer tube. This feature will separate the hydrogen in the sample from the rest of the gas and the helium carrier gas. The GC is equipped with a thermal conductivity detector using thermistors. The GC has been calibrated against a standard gas containing hydrogen, carbon dioxide, oxygen, nitrogen, methane, carbon monoxide. The other gases are approximated using an estimate of their proportionality factor.

In order to calibrate the GC we assumed that carbon monoxide possessed a K, a proportionality factor, was equal to one. This was caused by a limitation on the number of degrees of freedom on the set of equations used for the calibration. The basic equation used is

$$\text{Volume \% (I)} = \frac{K(I) * A(I)}{K(I\ ) * A(1)+K(2) * A(2)+. . ,+K(N) * A(N)}$$

where K(I), Volume % (I), and A(I) are the component proportionality constant, volume percent and the relative area for the 1-th component of N components. We know all the areas, the volume percents and the value of K for carbon monoxide. With this knowledge we can solve a set of five equations and five unknowns using simple linear can be viewed graphically more simply than it can be explained verbally. The sample network allows the evacuation of each sample bottle and separate sample collection. This is done independently of the other sample bottles. The sample bottles are only about 30 milliliters in volume and are constructed of tubing and fittings. All bottles were thouroughly leak tested. Each bomb connects to the network by means of a quick-connect fitting. This feature lets us capture a sample, seal it, and later inject it to the gas chromatograph for composition analysis.

The remainder of the gas now passes through a short section of TYGON tubing to two glass saturator bottles. These bottles are arranged so that if a vacuum is placed on the gas network by accident, no water will enter the sample network.

The saturated gas now enters a Precision Scientific three liter Wet Test Meter. The wet test meter has a thermometer and a mercury manometer attached to it for monitoring gas temperature and pressure. Gas leaving the wet test meter is vented to the atmosphere.

El^A^ęaROMĄTĄaKĄPH-SISTEM

The gas composition from each sample of a run is analyzed with a Carle 1 11H gas chromatagraph (GC) which is algebra. The value of K has been placed in tabular form in Appendix A, Table 26.

The gas samples are injected into the one milliliter sample loop by first evacuating the sample system and sealing it off at about 29 inches of vacuum. The sample can then be sent into the loop and injected without fear of contamination.

The GC uses a Houston Instruments Model // 150 strip chart recorder with a sweep integrator. This allows each peak to be integrated and placed into the GC mass balance computer program.

G) COAL ANALYSIS SYSTEM

The coal sample and the char samples were analyzed for proximate analysis values with a Model 490 Fischer Coal Analyzer. We used 10 milliliter Airtight Quartz crucibles that release volatiles, but do not allow oxygen back into the crucible during devolatilization. The analyzer is equipped with a microprocessor that controls all functions on the unit. The analyzer has separate programs for sparking and nonsparking coal devolatilization, ASTM ash, and Fischer ash preset programs. It also allows for user programable volatiles and ash analysis.

The nonsparking volatiles program was used to analyze the lignite and char for volatile content. This program heats the oven dried sample to 950 degrees Centigrade at 35 degrees Centigrade per minute and hold for seven minutes. The crucible covers are left on to keep the oxygen away from the sample.The furnace fan is off to reduce the air current which might enter the crucibles.

The Fischer ash program was used since we had already devolatilized our sample before checking the ash content. The devolatilized samples are heated to 750 degrees Centigrade at 35 degrees Centigrade per minute and held at that temperature for three hours with the crucible covers off. Also, the furnace fan is on to allow for improved air circulation.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The procedures for the operation of the unit and the analysis of the lignite, char and gas can be separated into proximate analysis, run of the experiment, and analysis of products. The data from some of these procedures are only useful for an individual experiment, but some will be used over a series of runs.

A2PROXIMAIE_ANALISIS

Preliminary analysis of the lignite must be done for use with the other gasification data and to know the fraction of water, volatiles, fixed carbon, and ash. The analysis of the lignite and char was performed per the instructions with the Model 490 Fischer Coal Analyzer, manual #43661. The lignite and char were dried in the oven at 107 degrees Centigrade for one hour. The volatiles were released using the non-sparking volatiles program with a furnace hold time of seven minutes. The fixed carbon and ash were determined using the Fischer Ash program with the crucible covers off as opposed to the volatiles analysis with the crucibles covered. The lignite proximate analysis was only done for several samples to begin with and was checked periodically for changes.

BJ_£LIA1LS_OE_PYROLISI£

The actual run of the experiment can be accomplished in approximately four hours, if no technical problems arise. The reactor must first be leak tested under pressure with the bottom of the reactor capped. After this the furnace can be put into place and the power turned on to begin heating the reactor. The helium is regulated to a maximum of 20 pounds per square inch (gauge) into the rotameter choke valve. The rotameter is adjusted for approximately 100 milliliters per minute of flow to purge the reactor and the rest of the system of air. When all the air is gone, in about ten to fifteen minutes, the flow rate should be set to ten milliliters per minute during the rest of the heating period.

While the reactor is heating, the lignite sample that has been ground to 0.25mm to 0.59mm particle size should be measured for use in the experiment. The sample size is very important. If the sample size is allowed to vary drastically, then the heat transfer characteristics of the lignite may change. Our goal was to use a sample size of 20 grams. This would make the bed size in the reactor 11.5

centimeters in depth. The sample is now sealed in a flask and set aside until time for sample injection.

The helium flow rate is verified by use of the wet test meter (WTM) over a five to ten minute period of time due to the slow rate of flow the carrier gas.

As the furnace begins to equilibrate, the final temperature should be checked and adjusted to the desired value. Next, a temperature probe is inserted to check the temperature profile of the furnace through the three thermocouple ports. Adjustments are made on the temperature controllers to bring all three zones of the furnace to the same temperature.

All gas sample bombs are attached to the sampling network and evacuated. This allows for rapid sampling of the product gas during the run.

The unit is now ready for the sample to be placed in the hopper. The hopper must be purged of as much air as is possible by bleeding helium pressurized gases out of the hopper. The hopper is placed under positive helium pressure of 30 pounds per square inch (gauge) until sample injection. This will amount to approximately 0.28 liters of helium that will be subtracted from the total gas production.

Ice is now placed around the tar traps and the wet test meter is zeroed for the beginning of the experiment. If the reactor and furnace temperatures are stable, then the run is ready to begin.

All helium flow to the hopper is stopped, the hopper dump valve is opened, the timer is started, and run data is collected. Since most of the gas is evolved in the first few minutes for the medium and high temperature experiments, short interval data gathering is important. The reactor temperature, reactor pressure, and gas volumes are all checked every fifteen seconds for the first three minutes. After three minutes, readings are taken at intervals of thirty seconds. After ten minutes, the readings are taken at one minute intervals.

Gas samples are taken at different times during the run. Since the bulk of the gas is produced in about two to five minutes, one sample is gathered at one minute, another at two and one-half minutes, the next one at seven minutes, and the last at ten to twelve minutes into the run. This technique of gas sampling is used to estimate the average gas composition and thereby the average gas molecular weight of the gas produced.

The samples are taken by closing the vacuum manifold valve and opening the sample manifold valve. Next, the bomb valve is closed and the sample bomb feeder line is evacuated by reopening the vacuum manifold valve for a moment. The sample may now be removed at the quick-connect fitting. This fitting will allow the sample to be attached to the gas chromatagraph. See Figure 1 for more information on the sample valve arrangement.

At twenty minutes the furnace is turned off and rolled away from the reactor. Cooling occurs rapidly after the furnace is removed. As soon as possible, after the reactor is below 200 degrees Centigrade, the tar traps are removed and the reactor is sealed with a cap fitting. The helium carrier is turned off. The tar traps are removed together and are sealed for later weight analysis. When the reactor is below 100 degrees Centigrade, we open the reactor and pour the granular char into a pre-weighted screw top bottle. The char will be reweighed in the bottle to obtain the weight of the char. All of the materials are now collected and now must be analyzed.

O._EK0ШI£1_A&Aкт£

The products are in three forms: char, tar and gas. These will be discussed, in order, with emphasis on the gas chromatography procedures.

The char from each run is weighed and subjected to a full proximate analysis to determine the amount of volatiles remaining, the fixed carbon content, and the weight of ash. The procedure for this is referenced in this chapter under the preliminary analysis section for the lignite proximate analysis.

The tar traps are disassembled and each piece is weighed with the tar still in place. Then the parts are cleaned with methylene chloride and methanol. After each part is cleaned, it is air dried and reweighed. The sum of the difference is the amount of tar and water from that run.

The gas in each sample bomb must also be analyzed for the composition of the gas. The Carle Model 1 1 1H Analytical Gas Chromatagraph is operated as per the operating procedures in the Carle manual for this unit, part number 30491. The operation of the sample injection system is not complex, but must be understood to be operated properly and accurately.

The injection system is drawn in Figure 2. The sample loop consists of the one milliliter internal gas chromatograph loop, the vent line to the valve, the sample line to the sample bomb quick-connect, and the sample line to the standard gas valve. All of the sample loop must first be evacuated by opening the vacuum line valve. After the loop is fully evacuated, the vacuum valve may be closed. The sample bomb valve is cracked to allow the gas to bleed into the sample loop. The sample must be the same in size. This is accomplished by bleeding the sample into the evacuated sample loop until the pressure is 15 inches mercury of vacuum. At this time, the sample is ready to be injected. The valve switching for the GC may be found in the previously mentioned Carle manual.

CHAPTER V

RESULTS AND DISCUSSION

The experimental results from the fifteen usable experiments will be presented for discussion purposes in graphical form in Appendix B and again in tabular form in Appendix A. The graphs will be displayed in two formats. The first will be used to display such items as material balance data and will be plotted versus final reactor temperature. The second type of format will be plotted against real time and used for reactor temperature recovery and gas evolution rate.

The data will be presented and discussed in two sections. The material balance data will come first and can be broken into four categories: lignite, char, tar, and gas data. The other section contains the normalized temperature and volume histories for each experiment.

The results from our experiments were gathered over a range of reactor temperatures from 413 degrees Centigrade to 937 degrees Centigrade. The sample size injected to the reactor varied greatly during some of the early runs. The problem was caused by insufficient hopper pressure which was used to break the packed formation of the coal in the hopper after the valve was opened. The sample size variation may be one of the contributing factors to the scatter of our data. This will be further discussed later in this chapter. The devolatized gases were swept from the reactor by helium flowing downward through the lignite at approximately 10 cubic centimeters per minute STP and by the escaping gas and liquid phase volatiles.

ál_M¿terial Balance

In this discussion of the material balance data, comparisons will be made on the basis of the initial grams of volatiles and fixed carbon in the lignite. The use of a dry-ash-free (DAF) basis for the mass balance comparisons is very useful since this commmon factor will standardize the grams of char, tar, and gas produced.

Li_LignLtė_Dala

The Mississippi Lignite used in these experiments came from the Tocowa seam in Panola county, SE 0.25 Section 8-10S-8W. The lignite was ground by hand, as it is soft, and sieved to a partical size of 0.25mm to 0.59mm and a small portion to a larger size of 1.00mm to 1.41mm. After grinding, the appearances of the lignite is much the same in color as before in its raw state. The ground lignite is a medium to dark brown and appears much like fresh coffee in texture and color. The sample of lignite was analyzed by proximate analysis on a Fischer Coal Analyzer, the results appear in Appendix A, Table 1.

Even after the ground lignite was mixed, some heterogeneous characteristics were inferred by scatter of the proximate analysis data. The actual proximate analysis data appears in Table 2.

2_1_Çhân_Dala

The char removed from the reactor flows easily and appears to be sized the same as the ground lignite injected to the bed. The only difference in appearance is the obvious change in color from brown to black.

Figure 3 contains the total carbonaceous material data as prepared by proximate analysis of the char on a gram per gram dry ash free (DAF) basis. As can be seen in Figure 3 the amount of total carbonaceous material on the char does apppear to decrease as final reactor temperature increases. In order to check where this changed is coming from we must first look at Figure 4 to see that no significant change has occurred in the fixed carbon content of the char as the temperature was increased. If we now look on to Figure 5, the 20% change in total carbonaceous material on the char per gram DAF must be a result of volatiles.

One noticable point in the char data is the grams per gram DAF coal of fixed carbon in the char and in the lignite. The lignite contains 0.309 grams of fixed carbon per gram DAF coal which is different from the char at 0.39 gram per gram DAF coal on the average (Figure 4 and Table 1, Appendix A). This redeposition of heavy volatiles before they can escape from the particle as noted by Anthony, Howard, Hottel and Meissner (11) may be caused by our slow heating rate. It is interesting to note, in Figure 4, that the amount of fixed carbon does not change with temperature. Larger particles have a slower heating rate and a longer diffusional path, therefore a longer volatile residence time in the particle as suggested by Anthony, Howard, Hottel and Meissner (11). The data in Figure 4 and Figure 5 may show that more volatiles are deposited on the char as fixed carbon, but additional data would be required to substantiate this hypothesis. This leaves less volatiles to escape from the char under proximate analysis. Since we only have one large particle data point and the large particle lignite is 2.4% higher in fixed carbon content than the comparable smaller particle runs, it is not possible to be certain that this is the cause of the change in fixed carbon.

Another point of interest in Figures 3 and 5 is the lack of extra volatile release above about 700 degrees Centigrade. The fact that this is happening may be support for a heating rate limitation in either the particle or in the reactor.

3) Tar Data

The apperance of the tar gathered from the traps varied, but most of the sample was black with streaks of bright yellow solids and a small amount of condensed liquids in the bottom which we assumed to be water and hydrocarbons.

The tar data is some of the most scattered data from our experiments. This is possibly due to the means by which we trapped the tar. The tar only consists of a few grams of material, while the mass of each trap is near to 100 or more grams. By measuring small differences in large masses, error in tar measurement is unavoidable.

In Figure 6 we divided the grams of tar and water from each run by the total grams of DAF lignite injected. Figure 7 is the same data with the estimated amount of water from the proximate analysis of the lignite removed from the tar. The amount of tar seems to be decreasing as the final reactor temperature increases. This would be expected since at a higher temperature more of the volatiles released would be cracked. The change in the tar production from the lower end of the temperature range to the higher end is from 40% to 20% tar per gram DAF lignite.

The large particle experiment is lower in tar release than the other experiments. The effect of the large particle is again a supposition at best since the volatile content of the large particle lignite is 3% lower than the small particles and we only have a single run of this particle size. Also, the distance outside the 95% confidence limits is not far enough to be sure of a statistically justifiable difference from the rest of the data. This is, however, another possible piece of evidence for the secondary reactions of the volatiles.

Łi_Qas_DsŁa

The gas analysis is the most detailed and tedious part of the experiment. The gas data has been analyzed through the use of a specialized Gas Chomatagraph(GC) which will separate hydrogen from the helium stream. This allows the analysis of nitrogen in our gas phase and a positive hydrogen response curve. For more information on the GC, see the previous chapters on Materials and on Methods.

The volume of gas generated was measured with a three-liter wet test meter (WTM). Initial, periodic, and final gas readings were taken from the WTM. The data was corrected for helium flow, temperature, and pressure to STP. The volume of gas at STP is displayed in Figure 8 versus final reactor temperature. Figure 8 demonstrates that as the reactor temperature increases so does the volume of gas phase volatiles in contrast with the liquid phase volatiles caught in the traps.

The composition of the gas also changed with the temperature of the reactor. By taking several gas samples through a run we are able to estimate the average gas composition and therby the average molecular weight of the gas. In Figures 9, 10, 11, 12, 13, 14, 15, and 16 are the weight percent graphs of the components that our GC has been calibrated. The major gases of interest here are hydrogen, carbon dioxide, ethylene, nitrogen, methane, and carbon monoxide. These gases also comprise the major part of the total gas volume.

In the appropriate graphs, you can see that as reactor temperature increases all but a few of the gases changed in weight percent. Hydrogen, nitrogen, ethylene, methane, and carbon monoxide, all increase with increased reactor temperature. At the same time carbon dioxide is decreasing in concentration.

The most concentrated components on a weight percent basis are carbon monoxide and carbon dioxide (Figures 12 and 10). If we compare the concentration of these two gases we can see that as carbon monoxide increases, carbon dioxide decreases. The changes in gas production are apparent if comparisons are made on the basis of the total grams of a gas produced per gram DAF (Figures 17, 18, 19, and 20). The changes in the gas concentration are probably due to dilution of carbon dioxide by carbon monoxide, hydrogen and methane. The total grams of carbon dioxide remain the same with a large amount of scatter (Figure 18). The research by Ballantyne, Chou, Neoh, Orozco, and Stickler(17) indicated that most of the volatiles leave the char as heavy organics except for subsequent cracking and only a negligable amount of the volatiles evolved as gases. Therefore, the increase in carbon monoxide, hydrogen and methane are probably by secondary reactions of the volatile matter.

Concentrations of hydrogen sulfide and ethane in the gas have been plotted, but they are only found in trace amounts and the data are scattered. Hydrogen sulfide was detected in our experimentsover the range of 0.0 grams to 0.00205 grams per gram DAF coal. The amount of hydrogen sulfide produced seemed random in nature over the previously mentioned range.

An estimate of the gas molecular weight versus temperature is plotted in Figure 21. The molecular weight of the product gas declines as the final reactor temperature increases. The change in the molecular weight seems mostly due to the increase in the formation of carbon monoxide, methane and hydrogen.

If we look at Figures 8, 21, and 22, which are the grams of gas per gram DAF lignite, we can see the increase in the volume and mass of the gas produced. The molecular weight is also falling from 40 grams per gram-mole to about 20 grams per gram-mole as temperature increases.

If the larger particle size causes a slower heating rate, then it does not appear to have a significant effect on the volume of gas produced (Figure 8). There is, however, a small effect on the molecular weight and therefore the number of grams of gas per gram DAF coal. In

Figure 21, the molecular weight of the large particle experiment is appoximately 6 grams per gram-mole heavier than the molecular weight on the regressed line through the data. Since the volume of gas is the same and the molecular weight is higher, it follows that the number of grams per gram DAF is higher (Figure 22) for the large particle experiment. This type of behavior can be expected in light of Anthony, Howard, Hottel and Meissner (11). The larger diameter of these particle has allowed more time for cracking of the tarry volatiles inside the particle. Another effect with the larger particles is that the void volume has changed from 0.415 for the small particles to 0.370 for the larger particles. This will allow for a shorter residence time of the volatiles in the gas phase. With this in mind, it is possible to hypothesize the reason for the increase in gas with a higher molecular weight. This could mean that the volatiles are held within the larger particles, allowed to decompose, and then diffuse to the outside of the particle. At the outside with a slightly faster helium carrier rate and a smaller void volume, the volatiles would be swept from the heated zone more rapidly. If we look at the tabular data in Appendix A, Table 8A and 8B, we can see the average weight percents of the large particle run (#19 at 705 degrees Centigrade). The weight percent of hydrogen is 3-0 percent for the small particles, on the average, and 0.8 percent for the larger particles. Typically, the more decomposition, the more hydrogen that is produced. Therefore, less decomposition in the secondary reactions must be occuring. The other plots of gas composition show that the other gas compositions are not significantly different from other experiments (Figures 13, 14, 15, and 16).

Figures 23, 24, and 25 show the volume of gas produced over the course of several experiments. In Figures 23 and 24, two temperature groupings have been plotted to show the clustering of the volume data. Also, we can compare run number 19 at 705 degrees Centigrade (19-705) with the other runs of the same temperature range in Figure 23. If we look at 19-705 (large particle) with respect to the other runs, we can observe the relative closeness with the other runs.

Another aspect is the slope of the gas production curves. Run 19-705,in Figure 23, has the same final voulme per gram DAF, but the slope is lower indicating a slower gas production rate than any of the other comparable runs of the same temperature range. This piece of information seems compatible with what we already know, since we would expect slower devolatilization from a slower heat transfer rate. The other curves in Figure 23 show the changes in gas production rate in much the same way as the large particle run has already been shown in a previous figure.

In Figure 25, there is a definite increase in the rate of gas production and in the total gas volume with respect to final temperature. The driving force for heat transfer is the differnce in temperature. The larger the gradient, the more energy is brought into or out of the system.

B. Temperature History

The temperature history could be very important to the total gas, tar, and char produced. With the proper temperature history and residence time, it may be possible to optimize the type of product desired from the lignite.

The form of display chosen for this section and type of data is one that allow transposition to other methods of heating. The temperature has been divided by the final reactor temperature and plotted versus time. The volume in milliliters at STP has also been divided by the final volume or the end of run condition of each value. Both of these, the normalized temperature and normalized volume, have been plotted together on a scale from zero to one.

Each experiment has its own graph of temperature and volume history, with the exception of run 1 3-928. Run 13-928 fell victim to a chart recorder problem.

The graphs mentioned earlier are found in Figures 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, and 39. These are in order of ascending temperature. It is apparent that the temperature histories of some of the runs differ in shape, but most are very similar in appearance. The shape difference that appears in some of the runs below 900 degrees Centigrade are mostly caused by a slight changed in reactor design to prevent leaks and to allow easy access to the bed area. The new reactor has less resistance to heat transfer. Therefore, a faster bed heating rate.

If we look at the runs above 900 degrees Centigrade, we can see that the drop in temperature returns to all the experiments, even the ones with the new reactor. The new reactor was brought into use after experiment 13. The amount of reactor temperature drop may be a function of the lignite sample size. In Figures 35, 36, and 39 we can see the relationship between sample sizes of 26.5 grams, 11.7 grams, and 8.4 grams and with a maximum drop of 0.63, 0.72 and 0.73, respectively, for the set of data from the old reactor. The new higher temperature experiments have the same correspondence between sample size and initial drop. Figures 37 and 38 were injected with 11.7 grams and 16.9 grams and fell to 0.82 and 0.65 on the normalized scale respectively. This shows that, at least for the high temperature experiment, the with an increase in sample size there is a corresponding increase in reactor temperature drop.

In Figure 29 is displayed the larger particle experiment temperature and volume histories. The temperature recovery does not seem to be a function of the particle size. The only noticable difference that can be seen in Figure 29 is the change in the gas production rate. This phenomenon has already been mentioned earlier in the section on e xpe rimental gas data.

If we now move to the next set of experiments in Figures 29, 30, 31, 32, 33, and 3^ which are the 700 degree Centigrade range we can again see that the gas rate of production is higher for the first part of the run, but does continue to increase much less rapidly. The last set of data is the high temperature experiments in Figures 35, 36, 37, 38, and 39 in the range of 900 degrees Centigrade. These runs have the same gas production pattern, except that as the final temperature of the reactor has been increasing, the temperature and volume curves are converging more rapidly. At the highest temperature the gas stops almost as soon as the final temperature is reached. This value of temperature is in the range of the proximate analysis temperature of 950 degrees Centigrade for the devol itil iz ation step.

The result of this could be that with the correct temperature the volatiles can be released to completion almost instantaneously with only mass transfer as a as a limitation to volatile release. At the higher temperature the rate of heating the sample must be faster since the driving force is increased. This must indicate that all of the volatiles diffuse from the particle and react outside the particle since only a small amount of volatile matter remains on the char. The time delay for heat transfer in our reactor must make it possible for the volatile to leave the particle at all temperature since only about 3% of the volatiles are turned to fixed carbon.

CHAPTER VI

CONCLUSIONS

The examination of the experimental results indicates the following conclusions:

1) The amount of volatile content remaining appears to be an inverse function of the final reactor temperature below 700 degress Centigrade.

2) The volatile content remaining appears to be approximately constant with respect to final reactor temperature above 700 degrees Centigrade, as over 90 percent of the volatiles are removed.

3) The volume of gas generated per gram DAF coal increases with final reactor temperature.

4) The grams per gram DAF of carbon monoxide, methane, and hydrogen all increase with increased final reactor temperature, while carbon dioxide remains relatively constant with temperature.

5) The molecular weight of the gas decreases with the final reactor temperature.

6) The total grams of gas produced is increasing with respect to reactor temperature.

CHAPTER VII

RECOMMENDATIONS

The results of this study indicate the need for the following recommendations for further research:

1) Reduce the bed mass to increase the heating rate and to decrease the chance of secondary reactions of the volatil es ;

2) Run several sample sizes (bed depths) to investigate the affect of volatile residence time on the char;

3) Change the gas flow rate to sweep the volatiles from the bed more rapidly;

4) Try several other particle sizes and investigate the affect on the gas composition; and

5) Try several moisture contents to observe the effect on the temperature history and the effect on the product yield.

BIBLIOGRAPHY

1. Luppens, J. A., "Exploration for Gulf Coast United States Lignite Deposits: Their Distribution, Quality, and Reserves," paper presented at Second International Coal Exploration Symposium, Denver, Colorado, October 1-4, 1978.

2. T. Gary Williams, Mississippi Department of Energy and Transportation, Personal Communication, February 1983.

3. Agarwal, P. K., W. E. Genetti and Y. Y. Lee, "Pseudo Steady State Receding Core Model for Drying with Shrinkage of Low Rank Coal." to appear in Chemical Engineering Communications. 1984.

4. Schmitt, R. W., Journal of the Institute of Energy, 63 (June), p. 63 (1981).

5. Brown, F., Hydrocarbon Processing, 56(2), p. 361 (1977).

6. Paulson, 0. L. and T. R. Stuart, "Summary of Mississippi Mineral Resources", Resource Information Circular No. 61. The Mississippi Mineral Resources Institute, the University of Mississippi, 1979.

7. McCown, M. S. and D. P. Harrison, Fuel, Vol. 61 (November), p. 150 (1982).

8. Jung, K. and B. R. Stanmore, Fuel, Vol. 59, 1980, p. 74.

9. Agarwal, P. K., W. E. Genetti, Y. Y. Lee and S. N. Prasad, "A Model for Drying Fluidized Bed Combustion of Wet Low Rank Coals," to appear in Fuel, 1984.

10. Wen, C. Y. S. Dutta, "Solid-Gas Reactions in Coal Conversion Processes,"

11. Anthony, D. B., J. B. Howard, H. C. Hottel and H. P. Meissner. Fifteenth Symposium (Internation) on Combustion, The Combustion Institute, Pittsburgn, PA, 1975, p. 1303.

12. Walker, P. L., Jr., Personal Communication from A. J. Moffat, Phillips Petroleum, 1982.

13. Felder, R. M., C. C. Kau, J. Ferrell, and S. Ganesan, "Rates and Equilibria of Devolatilization and Trace Element Evolution in Coal Pyrolysis," EPS Project Summary, EPA-600/S7“82-027, Industrial Environmental Research Laboratory, Research Triangle Park, N. C., September 1982.

14. Scaroni, A. W. , P. L. Walker, Jr. and R. H. Essenhigh, Fuel, Vol. 60, (January) 1981, p. 71 .

15. Suuberg, E. M., W.A. Peters and J.B. Howard, I&EC Process Design and Development, 17(1), p. 37 (1 97 8).

16. Suuberg, E. M., W.A. Peters and J.B. Howard, Fuel, 59 (June) p. 405 (1980).

17. Ballantine, A., Chen, H., Neoh, K., Orozco, N. and Stickler, D., Proceedings of the ACS Division of Fuel Chemistry, 29 (2), p. 119 (1984)

18. Franklin, H. D., Peters, W. A. and Howard, J. B., Fuel, 61 (November) p.155 (1982).

19. Morris, J. P. and Kearins, P. L., Fuel, 58 (June) p.466 (1 979).

20. Nsakala, Y. N., Essenhigh, R. H. and Walker, Jr., P . L. , Fuel, 57 (October) p. 606 (1 97 8).

APPENDIX A

TABULATED DATA

Table 1 Average Proximate Analysis of Lignite

	Small Particles (0.25-0.59mm)	Large Particles (1.00-1.41mm)
Water	8.5%	8.1%
Volatiles	40.5%	42.1%
Fixed Carbon	18.1%	21.2%
Ash	32.9%	28.8%

Table 2 Mississippi Lignite Proximate Analysis Data

Sample	Percent Water	Percent Volatile	Percent Fixed Carbon	Percent Ash
1	10.06	47.79	23.29	28.92
2	10.19	46.38	21.46	32.16
3	10.14	48.91	20.57	30.52
4	6.87	42.71	17.34	39.95
5	6.M3	39.96	16.23	37.38
6	10.16	47.68	18.62	33.70
7	10.13	48.12	19.03	32.35
8	9.91	37.92	21.07	31.11
*9	8.13	42.10	21.30	28.40
*10	8.09	42.00	20.70	29.10

* Indicates Large Particle (1.00mm-1.41 mm)

Table 3 Proximate Analysis by Weight Percent

Region	Moisture	Volatiles	Fixed Carbon	Ash
Texas Lignite(14)		45.9	43.8	10.3
Louisiana	31.3	23.7	32.6	12.5
Lignite(7)		34.4	47.4	18.2
N. Dakota Lignite(20)		43.7	43.3	8.0
Wyoming Subbituminous(19)		46.1	50.4	3.4
Pittsburgh Seam Coal	2.0	36.2	51.0	10.4
Bituminous(18)		37.1	52.3	10.6

Table 4 Ultimate Analysis by Weight Percent

Region	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Texas Lignite(14)	71.6	5.3	1.4	1.6	20.0
Louisiana Lignite(7)	68.2	5.1	1.8	1.1	23.7
N. Dakota Lignite(20)	71.0	4.9	1.6	0.6	21.9
Wyoming(19) Subbituminous	73.3	5.0	1.23	0.5	16.5
Pittsburgh Seam Coal Bituminous(18)	82.9	5.7	1.3	2.9	7.2

Table 5 Char Proximate Analysis

Run Number	Sample Number	Percent Volatile	Percent Fixed Carbon	Percent Ash
5	1	6.14	25.18	68.68
5	2	3.95	15.53	80.52
6	1	2.27	17.43	80.30
6	2	2.90	22.84	74.26
7	1	4.03	34.92	61.05
7	2	4.94	32.72	62.35
3	1	5.73	33.05	61.23
8	2	5.25	32.58	62.16
9	1	4.37	37.63	58.00
9	2	4.72	36.19	59.10
10	1	14.72	34.54	50.75
10	2	15.30	33.56	51.14
11	1	12.94	33.29	53.78
11	2	18.76	33.29	47.95
12	1	24.83	29.04	46.13
12	2	23.80	28.23	47.97
13	1	7.68	34.94	57.38
13	2	7.31	36.22	56.47
14	1	15.04	30.17	54.80
14	2	8.18	36.29	55.53
14	3	5.38	39.13	55.50
15	1	3.59	37.37	59.04
15	2	3.47	37.89	58.64
15	3	2.57	35.83	61.60
16	1	3.32	33.39	63.29
16	2	2.87	32.81	64.82
16	3	2.51	30.08	67.41
17	1	9.55	34.18	56.26
17	2	7.27	34.64	58.09
17	3	7.06	35.02	57.92
18	1	5.40	37.20	57.40
*19	1	4.79	44.11	51.10
*19	2	5.20	43.45	51.35
*19	3	4.97	43.82	51.21

Table 6A Material Balance Data by Run-Temperature

Run-Temperature (C.)	Grams Gas	Grams Volatile	Grams Fixed Carbon	Grams Tar and Water
12-397	0.0816	0.3133	0.3687	0.3882
10-550	0.1416	0.1620	0.3682	0.4195
11-575	0.1887	0.1859	0.3918	0.4945
»19-705	0.4055	0.0429	0.3756	0.2584
6-710	0.2806	0.0286	0.2214	0.5468
5-734	0.2791	0.0585	0.2397	0.4393
17-752	0.3068	0.0791	0.3421	0.3382
18-769	0.2406	0.0439	0.3021	0.2552
16-774	0.2817	0.0296	0.3269	0.2567
9-816	0.3426	0.0458	0.3759	0.4032
13-928	0.3863	0.0900	0.4274	0.3704
7-930	0.2101	0.0370	0.2776	0.1364
14-930	0.4057	0.0577	0.2139	0.3606
15-934	0.2764	0.0285	0.3292	0.2623
8-937	0.2640	0.0418	0.2495	0.1271

Note: Numbers correspond to grams/gram DAF Coal

* Indicates large particle (1.00mm-1.41mm)

Table 6B Material Balance Data by Run-Temperature

Run-Temperature (C.)	Molecular Weight Grams per Gram Mole	Total Carbon Material Grams per Gram DAF	Total Liters Gas (STP)	Tar Grams per Gram DAF
12-397	¿40.6	0.6820	0.04913	0.2738
10-550	36.4	0.5302	0.09519	0.3051
11-575	36.4	0.5777	0.12680	0.3799
*19-705	29.5	0.4184	0.29600	0.1301
6-710	22.0	0.2500	0.31200	0.4324
5-734	21.3	0.2982	0.32020	0.3180
17-752	22.6	0.4212	0.3233	0.1557
18-769	17.6	0.3459	0.30120	0.0871
16-77^	22.4	0.3566	0.2707	0.0742
9-316	21.1	0.4218	0.3972	0.2888
13-928	20.6	0.5174	0.40160	0.2559
7-930	12.8	0.3145	0.40150	0.0220
19-930	20.5	0.2716	0.42530	0.2462
15-934	18.4	0.3577	0.27750	0.0819
8-937	15.5	0.2913	0.41670	0.0127

* Indicates large particle (1.00mm-1.41 mm)

Table 7 Grams Gas per Gram Daf by Run-Temperature

Run-Temperature (C.)	Hydrogen	Carbon Dioxide	Methane	Carbon Monoxide
12-397	0.000023	0.08974	0.00125	0.00791
10-550	0.000958	0.22613	0.01101	0.02603
11-575	0.000325	0.08748	0.00500	0.01324
*19-705	0.003821	0.27500	0.04989	0.11405
6-710	0.003982	0.07315	0.01877	0.02441
5-734	0.005285	0.08836	0.02777	0.03303
17-752	0.014713	0.29290	0.07167	0.06021
18-769	0.032711	0.18237	0.01894	0.09400
16-774	0.015616	0.27960	0.06507	0.12030
9-316	0.011223	0.15592	0.05786	0.08750
13-928	0.008462	0.05500	0.03063	0.07169
7-930	0.074533	0.06189	0.07857	0.55035
14-930	0.035331	0.24139	0.11811	0.29350
15-934	0.023075	0.13715	0.11321	0.21490
3-937	0.053534	0.94448	0.10547	0.53350

Note: Numbers correspond to grams/gram DAF Coal

* Indicates large particle (1.00mm-1.41mm)

Table 3A Gas Weight Percent Data by Run-Temperature

Run-Temperature (C.)	Hydrogen	Carbon Dioxide	Methane	Carbon Monoxide
12-397	0.02	88.2	1.2	7.8
10-550	0.3	80.6	3.9	9.3
11-575	0.3	79.2	4.5	12.0
*19-705	0.8	58.7	10.6	24.3
6-710	3.0	55.8	14.3	18.6
5-734	3.0	51.0	16.0	19.1
17-752	3.1	61.0	14.9	12.5
18-769	5.2	29.0	15.0	40.5
16-774	3.0	52.9	12.3	22.8
9-816	3.1	43.6	16.2	24.5
13-928	4.1	26.3	14.6	34.3
7-930	9.1	7.5	9.6	67.0
14-930	4.4	29.8	14.6	36.2
15-934	3.7	22.2	18.4	34.3
8-937	6.0	10.6	11.8	59.8

* Indicates large particle (1.00mm-1.41 mm)

Table 8B Gas Weight Percent Data by Run- Temperature

Run-Temperature (C.)	Ethylene	Ethane	Hydrogen Sulfide	Nitrogen
12-397	0.2	0.2	0.2	2.2
10-550	1.7	1.5	0.2	2.4
11-575	1.1	2.0	0.3	0.6
*19-705	3.2	2.0	0.0	0.3
6-710	4.2	3.0	0.2	0.9
5-734	7.0	3.3	0.0	0.6
17-752	3.0	3.1	0.4	1.7
18-769	3.7	2.1	0.1	3.0
16-774	3.7	2.6	0.4	2.3
9-316	8.1	3.1	0.2	1.1
13-928	11.1	1.8	0.0	7.0
7-930	0.9	0.2	0.0	5.6
14-930	11.4	1.5	0.0	1.9
15-934	15.8	2.3	0.2	2.1
8-937	4.0	0.6	0.1	6.9

* Indicates large particle (1.00mm-1.41 mm)

Table 9A Gas Mole Percent Data by Run-Temperature

Run-Temperature (C.)	Hydrogen	Carbon Dioxide	Methane	Carbon Monoxide
12-397	0.41	81.27	3.04	11.29
10-550 ,	5.43	66.37	8.83	12.03
11-575	5.36	64.38	10.06	15.33
*19-705	11.57	38.60	19.17	25.11
6-710	32.51	27.48	19.37	14.40
5-734	31.76	24.54	21.17	14.44
17-752	33.72	30.16	20.26	9.71
18-769	43.65	11.07	15.74	24.29
16-774	32.62	26.15	16.72	17.71
9-816	31.85	20.36	20.81	17.98
13-928	37.33	10.88	16.62	22.31
7-930	57.22	2.14	7.55	30.09
14-930	39.23	12.08	16.27	23.06
15-934	33.83	9.23	21.03	22.72
8-937	45.97	3.69	11.30	32.72

* Indicates large particle (1.00mm-1.41 mm)

Table 9B Gas Mole Percent Data by Run-Temperature

Run-Temperature (C.)	Ethylene	Ethane	Hydrogen Sulfide	Nitrogen
12-397	0.29	0.27	0.24	3.19
10-550	2.20	1.81	0.21	3.11
11-575	1.41	2.38	0.32	0.77
*19-705	3.31	1.93	0.0	0.31
6-710	3.25	2.17	0.13	0.70
5-73^	5.29	2.33	0.0	0.45
17-752	2.33	2.25	0.26	1.32
18-769	2.22	1.18	0.05	1.80
16-774	2.87	1.88	0.26	1.79
9-816	5.94	2.12	0.12	0.81
13-928	7.22	1.09	0.0	4.55
7-930	0.40	0.08	0.0	2.52
14-930	7.26	0.89	0.0	1.21
15-934	10.32	1.40	0.11	1.37
8-937	2.19	0.31	0.05	3.78

* Indicates large particle (1.00mm-1.41 mm)

Table 10 Temperature and Volume Histories

Run no. 5 Temperature *73*^ Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	0.0	728.
2.10	162.07	687.
3.70	198.30	705.
8.30	245.92	730.
10.20	256.84	730.
13.90	273.07	732.
17.30	282.02	733.
20.00	291.89	739.

Table 11 Temperature and Volume Histories

Run no. 6	Temperature	710 Deg. C
T ime (Min.)	Vol urne (Liters) STP	Reactor Temperature (Deg. C)
0.0	0.0	71 8.
0.17		503.
0.33		540.
0.50		575.
0.66		600.
0. 33		603.
1.00		615.
1.11	67.20	
1. 17		617.
1.33		617.
1 . 50		617.
1 .60	83.33	
1.66		617.
1. 83		617.
2.00		617.
2.17		617.
2.20	112.59	
2.33		617.
2.50		630.
2.66		630.
2. 33		635.
3.00		645.
3.10	144.92	
3. 50		665.
3. 83		6 90.
4.00		701 .
4.15	190.34	
4.50		704.
4.70	206.42	
5.00		707.
6.00		712.
6.33	234.84	
8.25	256.40	
9.50	265.29	
17.90	2 84. 83	
20.00	2 86.40	712.

Table 12 Temperature and Volume Histories

Run no. 7 Temperature 930 Deg. C

T ime (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	915.
0.17		762.
0.33		6 87.
0.50		707.
0.60		776.
0. 83		829.
1.0		860.
1.17		891.
1.25	291.04	
1.33		894.
1.50		901 .
1.66		901.
1. 83		901.
2.00		901.
2.40	324.05	
2.50		907.
3.00		907.
4.00		91 4.
5.50	336.14	
7.10	337.95	
8. 00		929.
8. 80	341.00	
10.00		929.
11.30	345.65	
14. 80	355.77	
16.60	357.29	
1 9. 80	363.6 8	
20.00		930.
20.60	369. 45	

Table 13 Temperature and Volume Histories

Run no. 8 Temperature 937 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	935.
0. 17		6 81 .
0.33		80 4.
0.50		846.
0.66		86 0.
0. 33		87 4.
1.00		87 9.
1.17		910.
1.33		913.
1 . 50		915.
1.66		921 .
1. 83		924.
2.00		927.
2.10	326.36	
3.00	338. 43	930.
4.00		932.
5.00	339. 1 3	
6.00		936 .
6.90	345.76	
3.00		936.
9.70	350.98	
10.00		937.
14.30	364.91	
15.00		93 8.
16. 80	374.46	
20.00		937.
20.60	381. 95	

Table 14 Temperature and Volume Histories

Run no. 9 Temperature 816 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	318.
0.17		525.
0.33		567.
0.50		603.
0.66		639.
0.83		653.
1.0		664.
1.10	65.16	
1.17		667.
1.33		675.
1.5		681.
1.60	108.49	
1.66		687.
1.83		692.
2.17		692.
2.33		690.
2.35	144.97	
2.50		681.
2.66		675.
3.00		675.
3.33		690.
3.66		710.
4.00		756.
4.15	254.60	
4.80	284.99	
5.00		785.
6.00		796.
6.50	308.76	
8.00		807.
8.40	333.67	
9.70	341.05	
10.00		810.
12.10	349.78	
13.70	354.58	
17.30	360.31	
20.00	363.99	816.

Table 15 Temperature and Volume Histories

Run no. 10 Temperature 550 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	553.
0.17		400.
0.33		419.
0.50		433.
0.66		455.
0.83		469.
1.00		483.
1.17		483.
1.33		491.
1.50		497.
1.66		497.
1.83		505.
2.00		511.
2.33		511.
2.50	12.01	
2.66		511.
3.00		514.
3.33		517.
3.66		517.
4.00		519.
5.00		520.
5.50	28.79	
6.00	32.95	522.
7.00		525.
7.50	39.15	
8.00		525.
8.75	47.35	
9.00		536.
10.00	57.43	536.
12.50	68.18	
14.00	74.38	
15.00	77.68	545.
17.00	82.39	
18.75	82.83	
20.00	87.27	550.

Table 16 Temperature and Volume Histories

Runno. 11 Temperature 575 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	558.
0.17		455.
0.34		455.
0.50		461.
0.64	11.66	
0.66		477.
0.84		480.
1.00	15.28	
1.17		497.
1.34		503.
1.50	18.21	503.
1.67		508.
1.84		516.
2.00	19.26	516.
2.75	23.98	
3.00	27.01	525.
3.50	29.32	
4.00	32.88	533.
4.50	35.82	
5.00	39.38	537.
5.50	41.06	
6.00	45.25	
7.00	57.39	537.
8.00	67.65	
9.00	78.53	548.
10.00	83.15	555.
11.00	90.27	
12.20	95.43	
13.00	99.50	
14.00	103.49	
15.00	106.23	566.
16.00	108.96	
17.00	111.07	
18.00	113.17	
19.00	114.65	
20.00	116.13	575.

Table 17 Temperature and Volume Histories

Run no. 12 Temperature 413 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	397.
0.25		288.
0.42	10.16	
0.70		304.
0.80	11.21	
1.50	13.34	342.
2.00	13.12	359.
3.00	14.51	373.
3.50	15.51	378.
4.00	15.29	386.
5.00	17.28	392.
6.00	19.28	397.
7.00	21.28	401.
8.00	25.10	406
9.00	27.70	410.
10.00	30.92	412.
11.00	32.31	413.
12.00	34.91	
13.00	37.52	
14.00	38.90	412.
15.00	40.90	411.
16.00	41.07	
17.00	41.85	
18.00	43.24	
19.00	44.02	412.
20.00	44.80	413.

Table 18 Temperature and Volume Histories

Run no. 13 Temperature 928 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	
0.71	167.59	
1.15	223.32	
1.75	297.60	
2.15	325.33	
2.70	351.09	
3.15	366.6 5	
M.00	372.58	
5. 00	371. 87	
6.35	370.91	
9.00	369.03	
10.00	36 8. 32	

Table 19 Temperature and Volume Histories

Run no. 14 Temperature 930 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	937.
0.30	88.63	768.
0.70	187.69	798.
1.20	268.52	798.
1.50	316.41	809.
2.00	377.63	849.
2.50	410.19	898.
3.00	433.69	907.
3.60	443.49	914.
4.80	448.01	922.
5.50	450.14	924.
7.00	448.24	928.
8.00	446.97	929.
10.00	444.43	930.

Table 20 Temperature and Volume Histories

Run no. 15 Temperature 934 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	928.
0.20	83.83	608.
0.60	175.54	764.
1.10	236.32	788.
1.65	276.48	830.
2.00	294.39	877.
2.50	299.75	903.
3.05	299.90	912.
3.50	299.18	920.
4.50	294.50	928.
6.00	290.04	931.
7.00	287.42	932.
8.50	285.01	933.
10.00	282.61	934.

Table 21 Temperature and Volume Histories

Run no. 16 Temperature 774 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	760.
0.25	43.18	716.
0.50	67.06	714.
1.00	95.53	708.
1.50	119.18	705.
2.00	146.68	707.
2.56	174.13	716.
3.50	220.52	739.
4.00	235.48	749.
5.00	260.58	760.
6.00	270.25	767.
7.00	272.20	770.
8.00	274.15	772.
10.50	278.54	773.
12.50	280.50	774.
15.00	281.03	774.
16.00	282.02	774.
18.00	282.06	774.
20.00	283.06	774.

Table 22 Temperature and Volume Histories

Run no. 17 Temperature 752 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	762.
0. 1 5	31.60	746.
0.35	62.06	729.
0.60	85.90	713.
0. 90	107.51	710.
1.00	113.98	709.
1.30	133.40	70S.
1.50	145.25	708.
1.75	161.43	707.
2.00	177.62	706 .
2.50	203.41	709.
3.00	229.21	716.
3.60	239. 59	730.
4.00	26 8.77	733.
4.50	281.43	740.
5.20	298.29	744.
6.00	309.58	748.
7.00	316.30	750.
8.00	320.83	751 .
9.00	323. 1 8	751 .
10.00	327.17	752.
13.00	331.47	752.
15.00	330.69	751 .
1 8.00	331.16	752.
20.00	331.47	7 52.

Table 23 Temperature and Volume Histories

Run no. 18 Temperature 769 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	813.
0.50	129.24	755.
1.00	197.05	761.
1.50	226.19	766.
2.00	254.18	780.
3.00	287.42	779.
3.50	302.91	771.
4.50	304.30	770.
5.00	304.99	769.
6.00	304.10	769.
7.00	305.49	769.
8.00	308.02	769.
9.00	309.41	769.
10.00	310.80	769.
12.00	310.16	769.
16.00	312.31	770.
20.00	314.45	769.

Table 24 Temperature and Volume Histories

Run no. 19 Temperature 705 Deg. C

Time (Min.)	Volume (Liters) STP	Reactor Temperature (Deg. C)
0.0	000.00	703.
0.25	21.74	661.
0.50	33.65	659.
0.75	40.26	658.
1.00	47.63	659.
1.25	55.75	660.
1.50	64.63	661.
2.00	83.90	663.
2.50	107.71	668.
3.00	129.26	672.
3.50	154.58	678.
4.00	179.15	689.
4.50	198.42	698.
5.00	216.94	704.
6.00	241.11	715.
7.00	263.01	723.
8.00	276.58	728.
9.10	287.81	725.
10.00	293.89	714.
12.20	295.91	710.
14.20	300.36	707.
16.00	303.46	705.
18.00	306.39	704.
20.20	308.41	705.

Table 25 The Chemical Processes of Coal Pyrolysis

Product	Source	Process
1. Tar + Liquid	Weakly bonded clusters	Distillation + Decomposition
2. Carbon Dioxide	Carboxyl groups	Decarboxylation
3. Carbon Monoxide *	Carboxyl groups and Ether linkages	Decarbonylation
4. Carbon Monoxide**	Hetero-oxygens	Ring Rupture
5. Water	Hydroxyl groups	Dehydroxylation
6. Methane + Ethane	Alkyl groups	Dealkylation
7. Hydrogen	Aromatic C-H bonds	Ring Rupture

* Less than 500 degrees Centigrade
** Greater than 500 degrees Centigrade

Table 26 Gas Chromatagraph Proportionality Constants

Gas	Constant
Hydrogen	8.8518
Carbon Dioxide	0.8689
Ethylene	0.6615
Ethane	0.6871
Acetylene	0.6844
Hydrogen Sulfide	0.6700
Oxygen	1.2207
Nitrogen	1.0007
Methane	1.1088
Carbon Monoxide	1.0000

APPENDIX B

TABULATED DATA

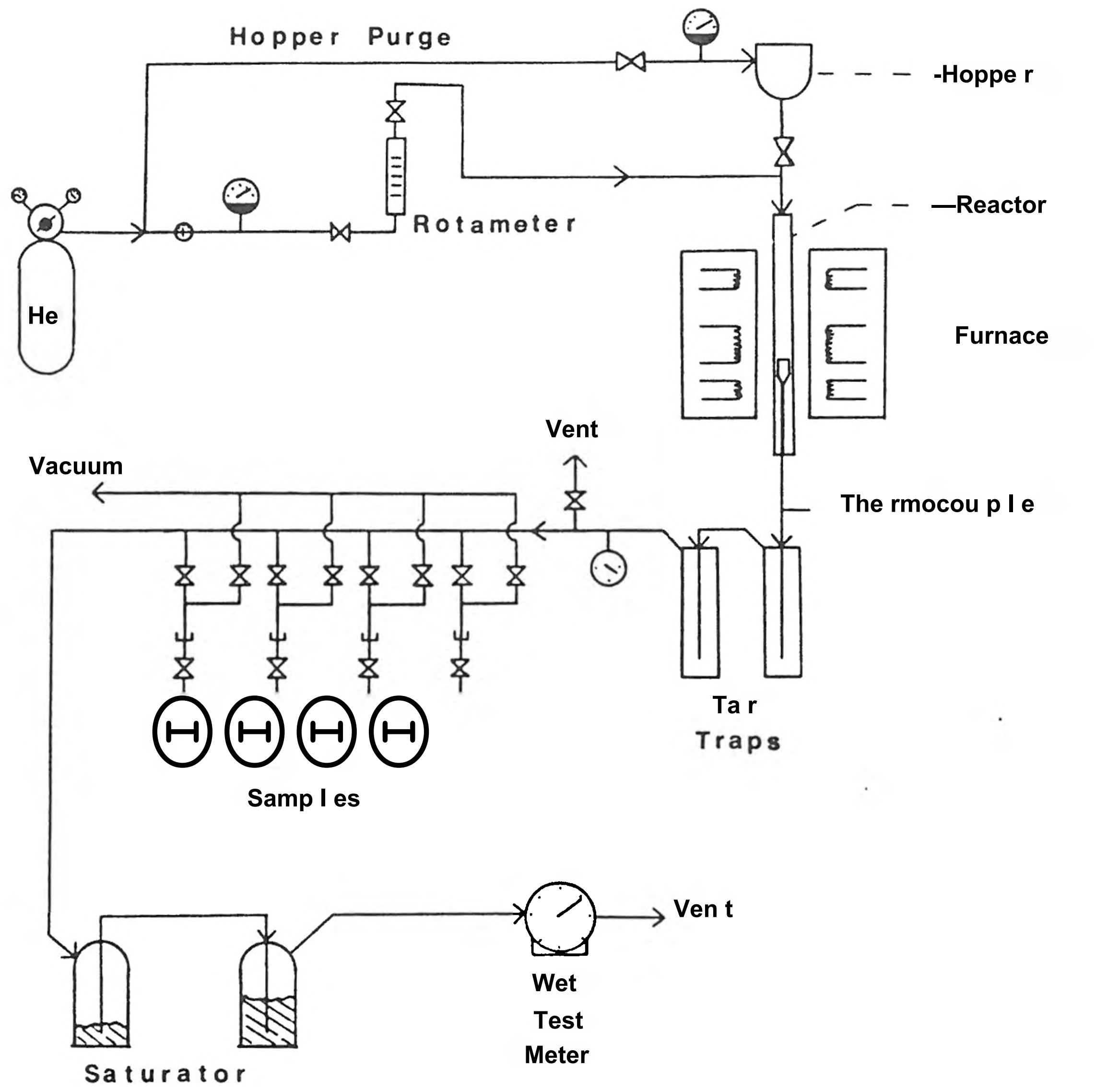


Figure 1: Reactor Piping Flowchart

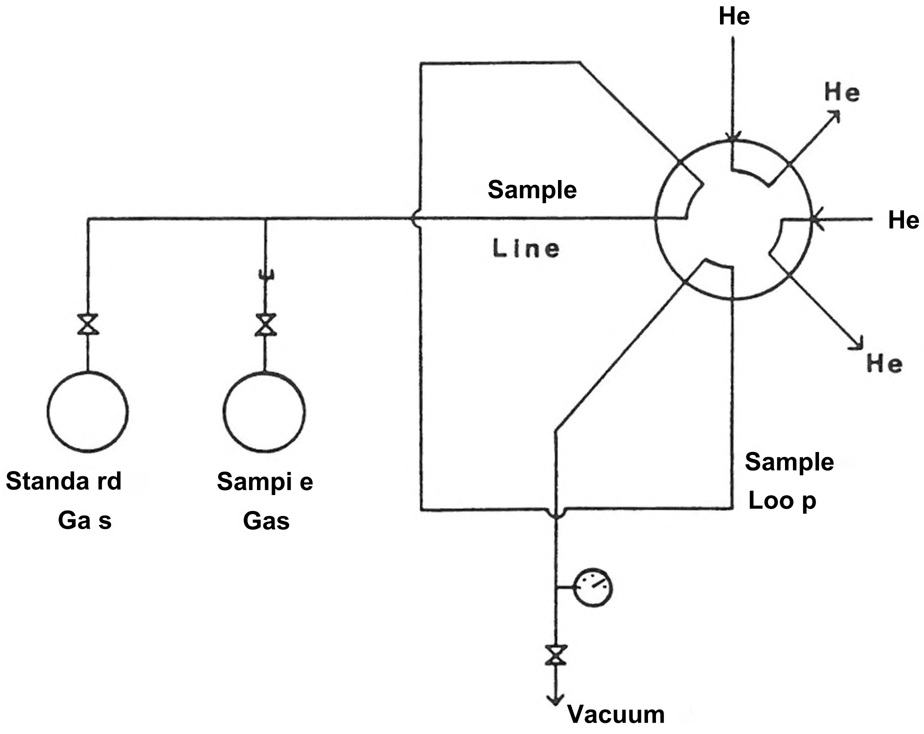
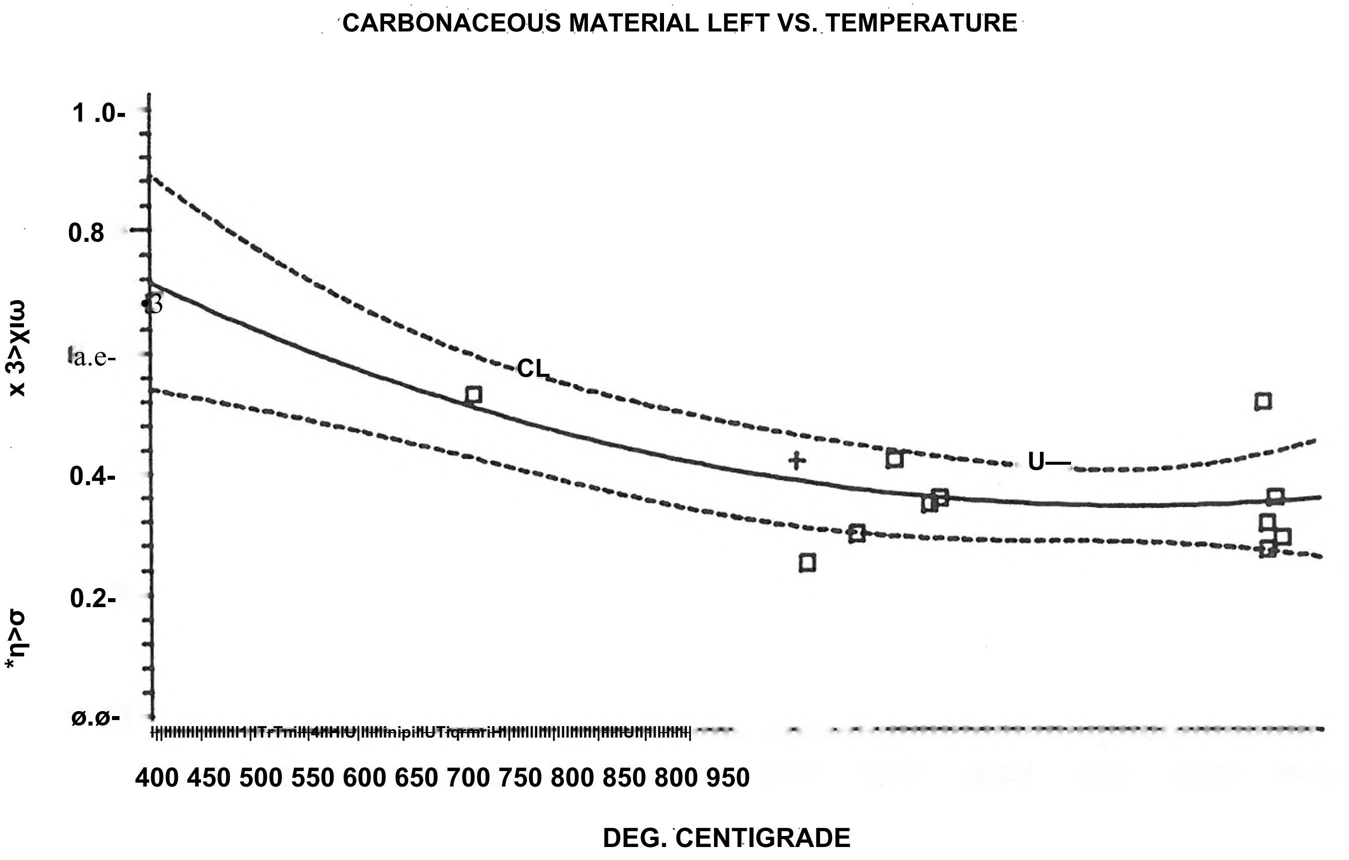


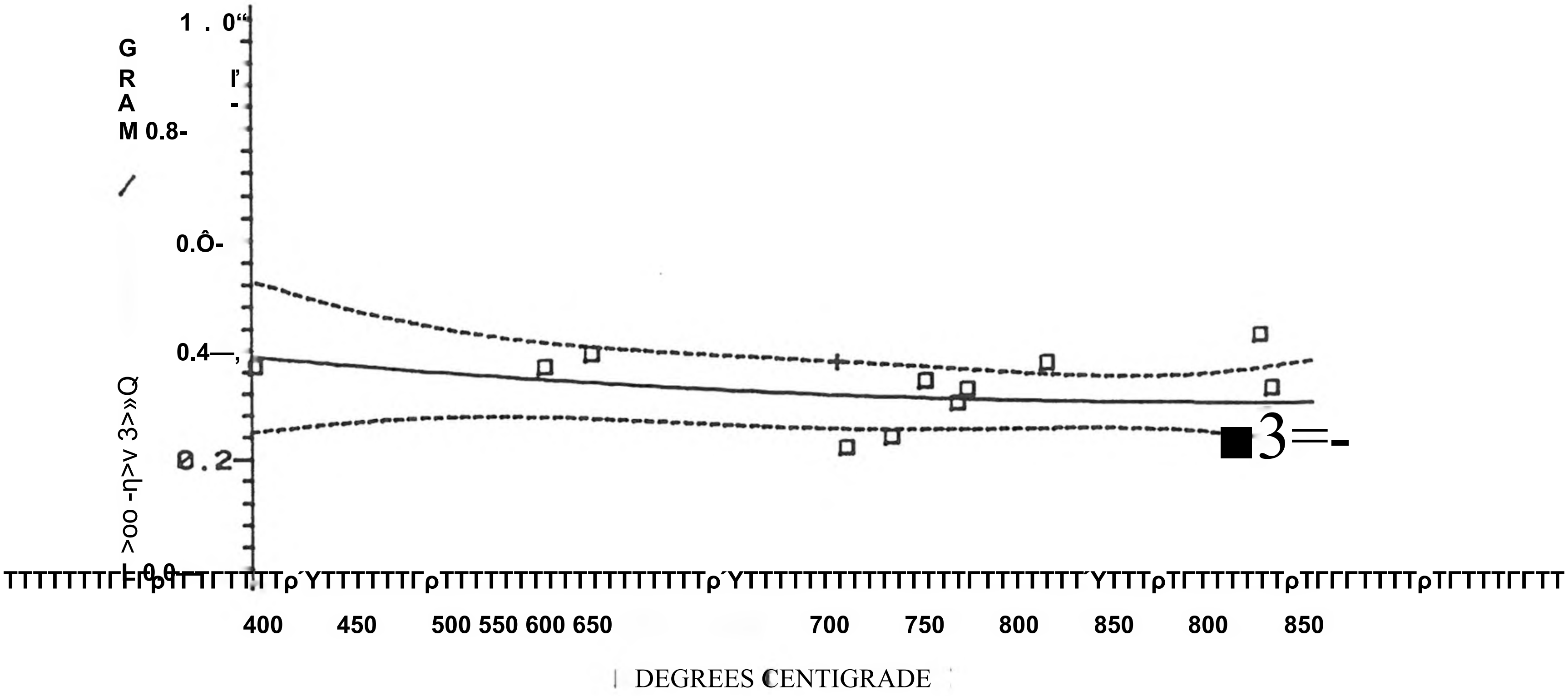
Figure 2. Eight Port Gas Chromatagraph Valve Shown in Counter Clockwisw Position (Sample). Sample Injection by Switching Valve to Clockwise Position (Inject).



NOTE: CARBONACEOUS MATERIAL / GRAM DAF COAL WITH 95 PERCENT CONFIDENCE LIMITS
SMALL PARTICLES(0.25MM-0.590MM): SQUARES
LARGE PARTICLES(1.00MM—1.41 MM): PLUS

Figure 3

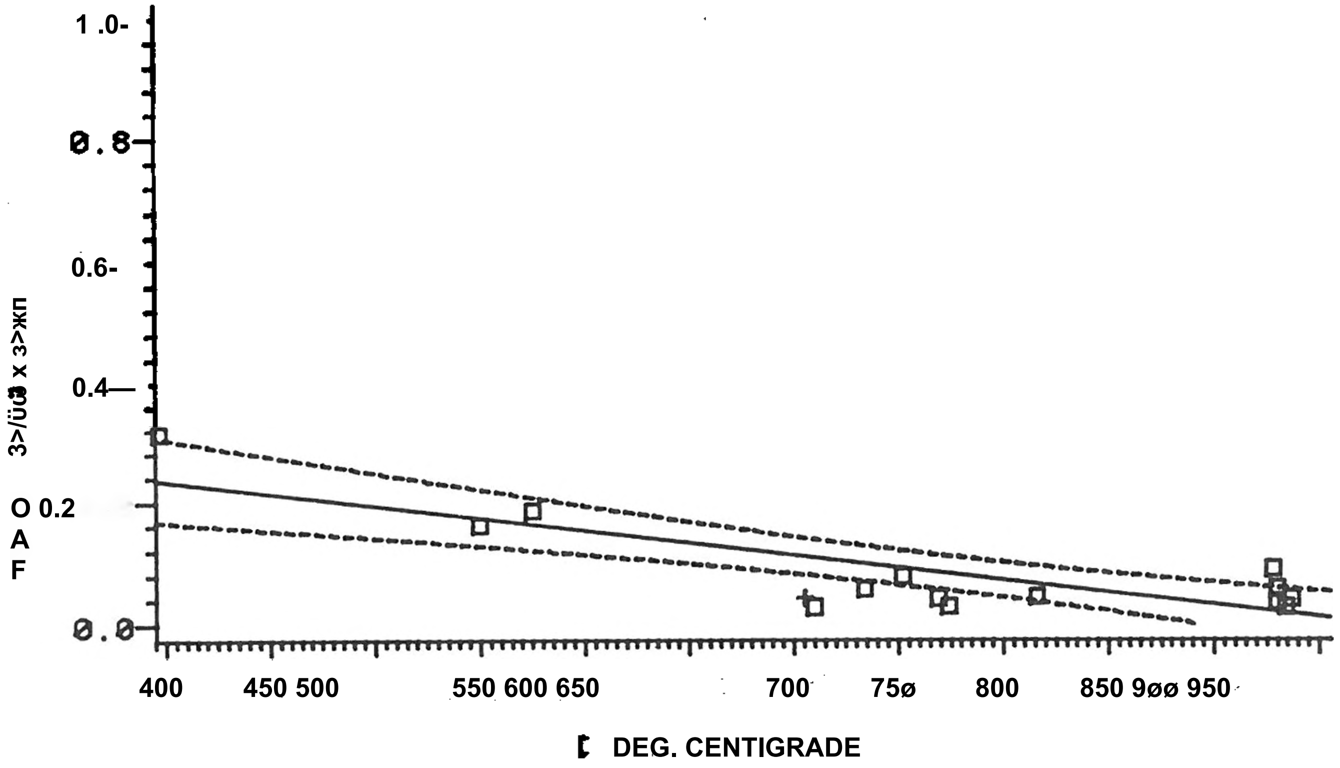
GRAMS FIXED CARBON IN CHAR / DAF COAL VS. TEMPERATURE



SMALL PARTICLES(0.25MM-0.59MM):SQUARE
LARGE PARTICLES(1.00MM-1.41MM):PLUS
(--------- 95 PERCENT CONFIDENCE LIMITS)

Figure 4

VOLATILE MATERIAL LEFT VS. TEMPERATURE



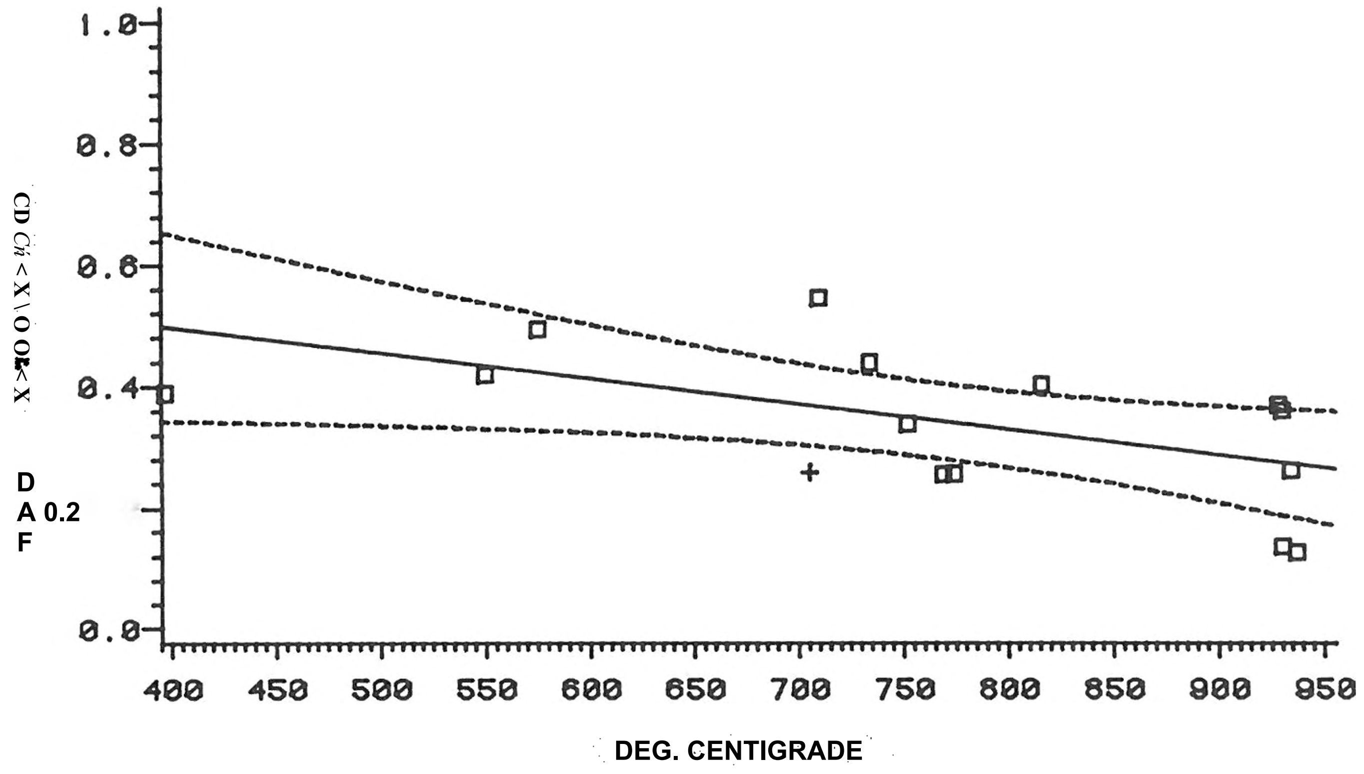
NOTE: VOLATILE MATERIAL / GRAM DAF COAL WITH 95 PERCENT CONFIDENCE LIMITS

SMALL PARTICLES(0.25MM-0.590MM): SQUARES

LARGE PARTTCLES(1.00MM-1.41MM): PLUS

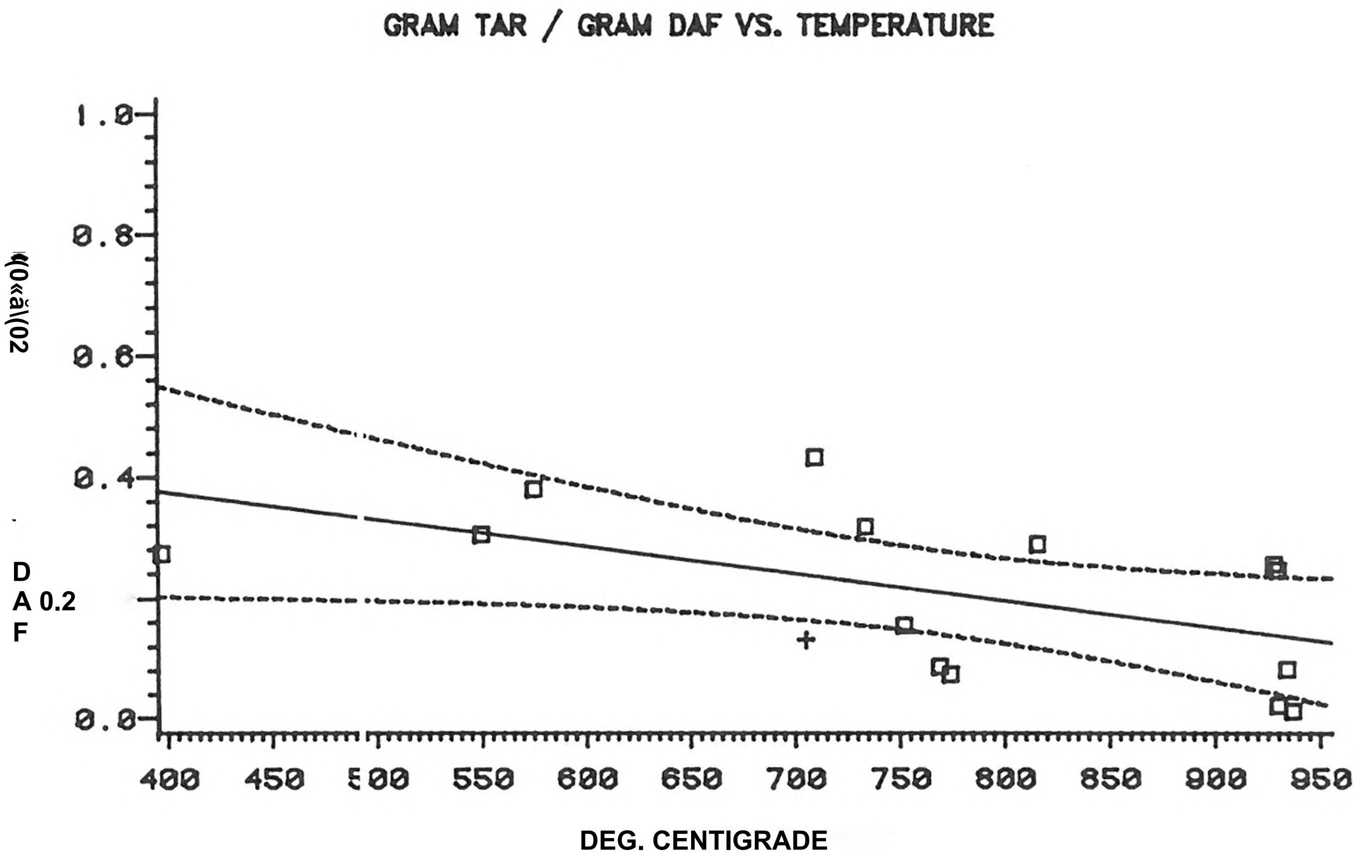
Figure 5

GRAM TAR AND WATER / GRAM DAT VS. TEMPERATURE



SMALL PARTICLES(0.25MM-0.59MM): SQUARES
LARGE PARTICLES(1.00MM-1.41MM): PLUS
(95 PERCENT CONFIDENCE LIMITS)

Figure 6



BMALL PARnCLES(0.25MM-0^9MM): SQUARES
LARGE PARTICLES(1.00MM-1.41MM): PLUS
(95 PERCENT CONFIDENCE LIMITS)

Figure 7

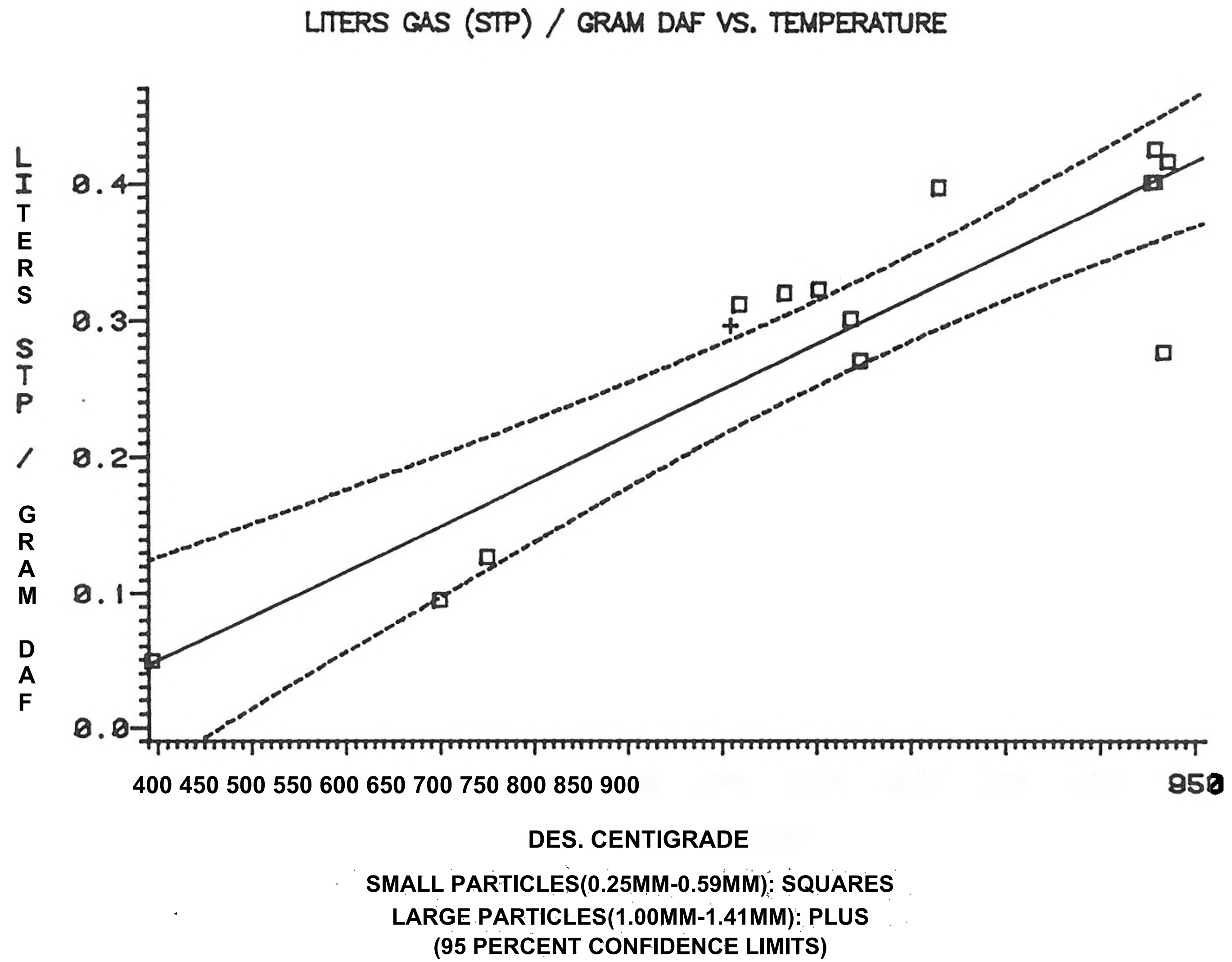

LITERS GAS (STP) / GRAM DAF VS. TEMPERATURE
LITERS STP / GRAM DAF
0.4
0.3
0.2
0.1
0.0
400 450 500 550 600 650 700 750 800 850 900
950
DES. CENTIGRADE
SMALL PARTICLES(0.25MM-0.59MM): SQUARES
LARGE PARTICLES(1.00MM-1.41MM): PLUS
(95 PERCENT CONFIDENCE LIMITS)

Figure 8

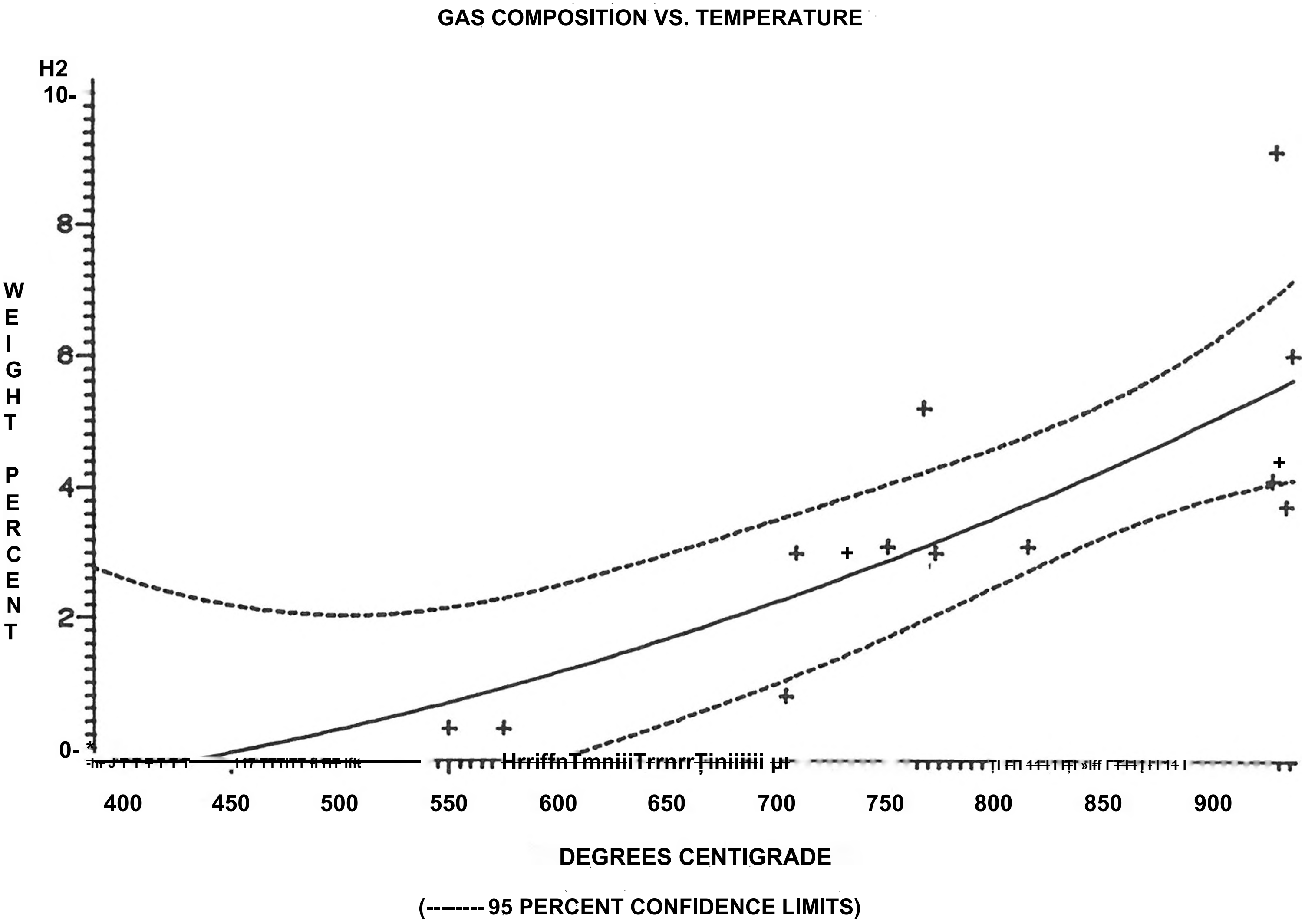
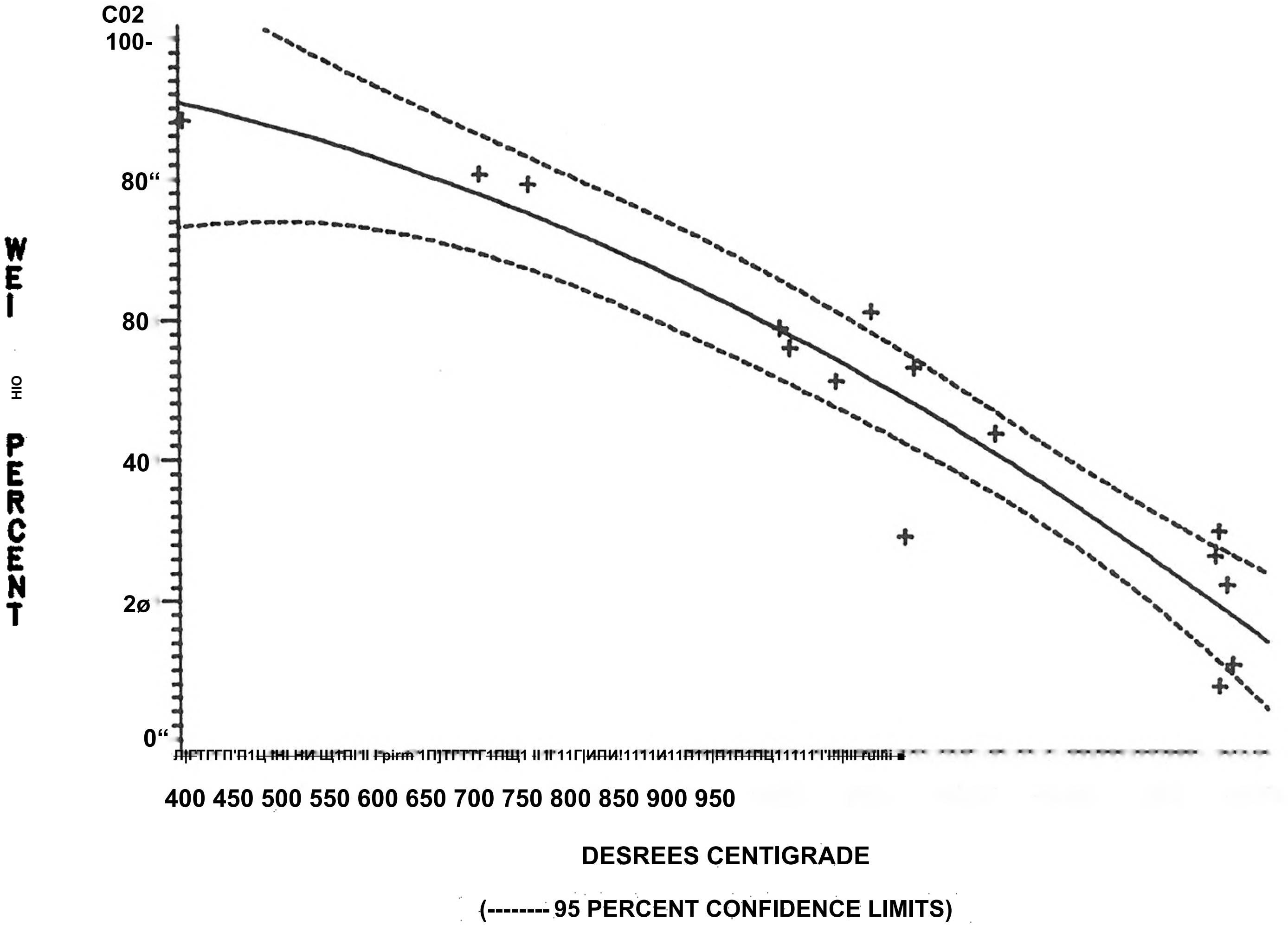

GAS COMPOSITION VS. TEMPERATURE
H2
10-
8
6
4
2
0-
WEIGHT PERCENT
400
450
500
550
600
650
700
750
800
850
900
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 9



GAS COMPOSITION VS. TEMPERATURE

Figure 10

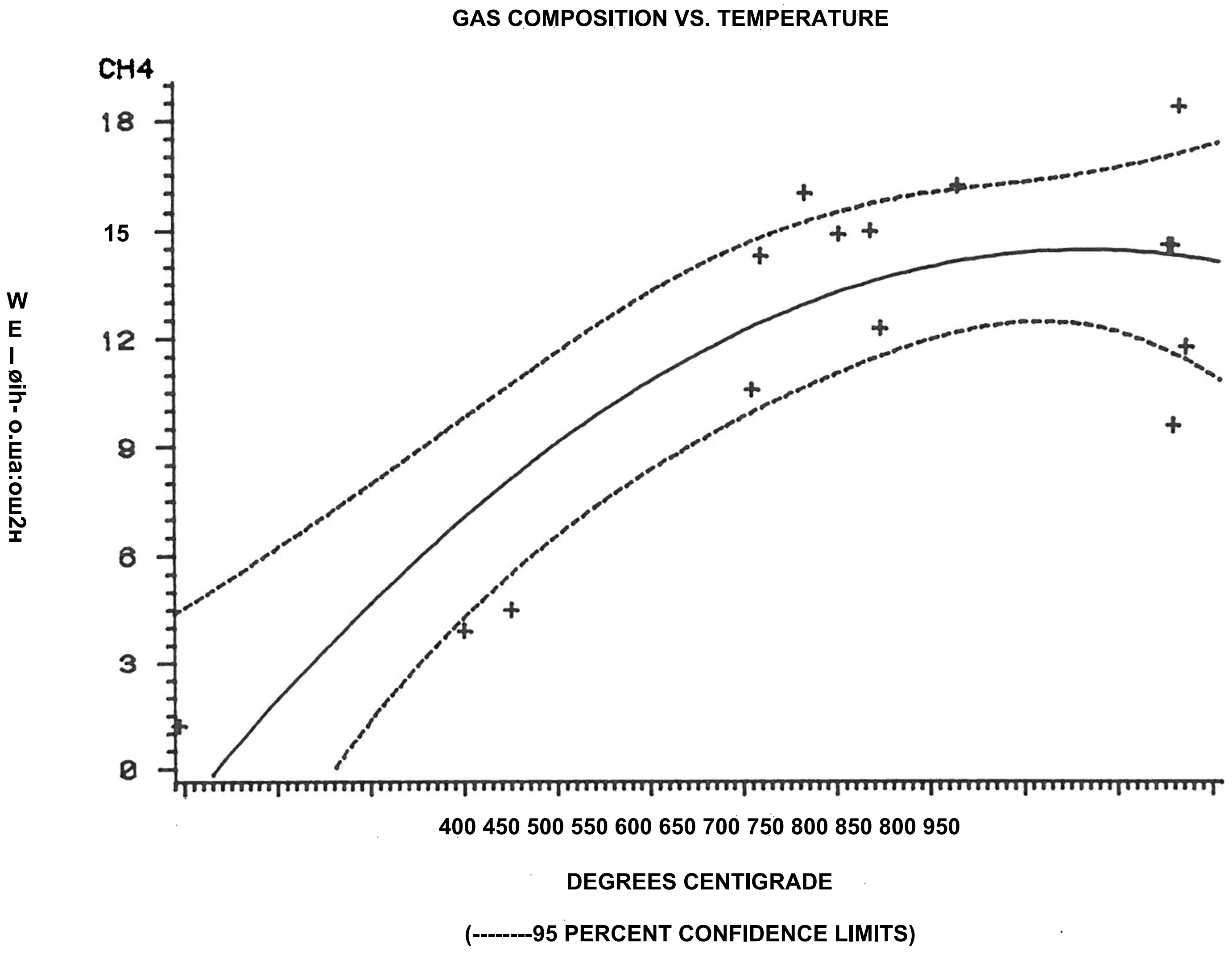
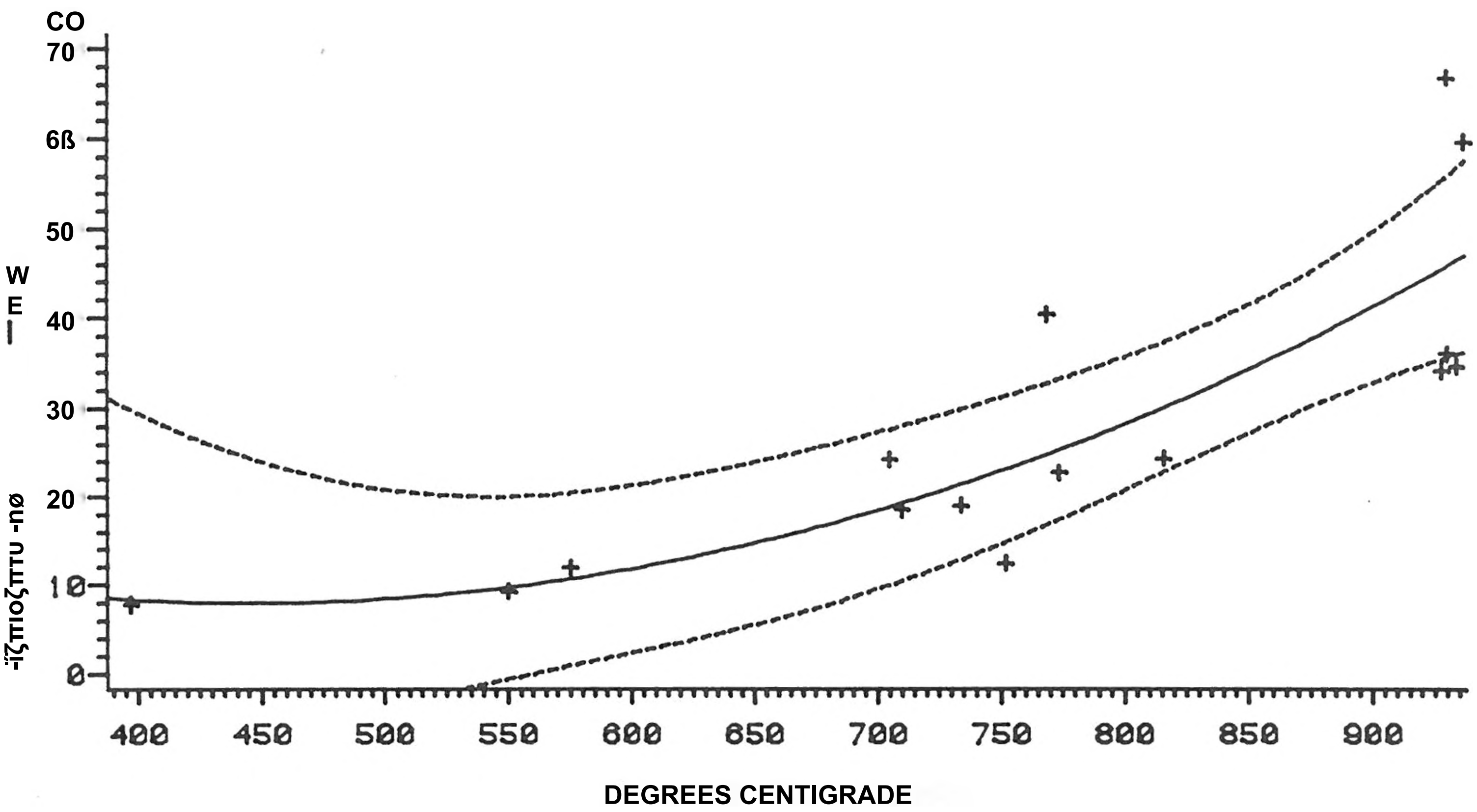

GAS COMPOSITION VS. TEMPERATURE
CH4
18
15
12
9
6
3
0
400 450 500 550 600 650 700 750 800 850 800 950
DEGREES CENTIGRADE
(--------95 PERCENT CONFIDENCE LIMITS)

Figure 11

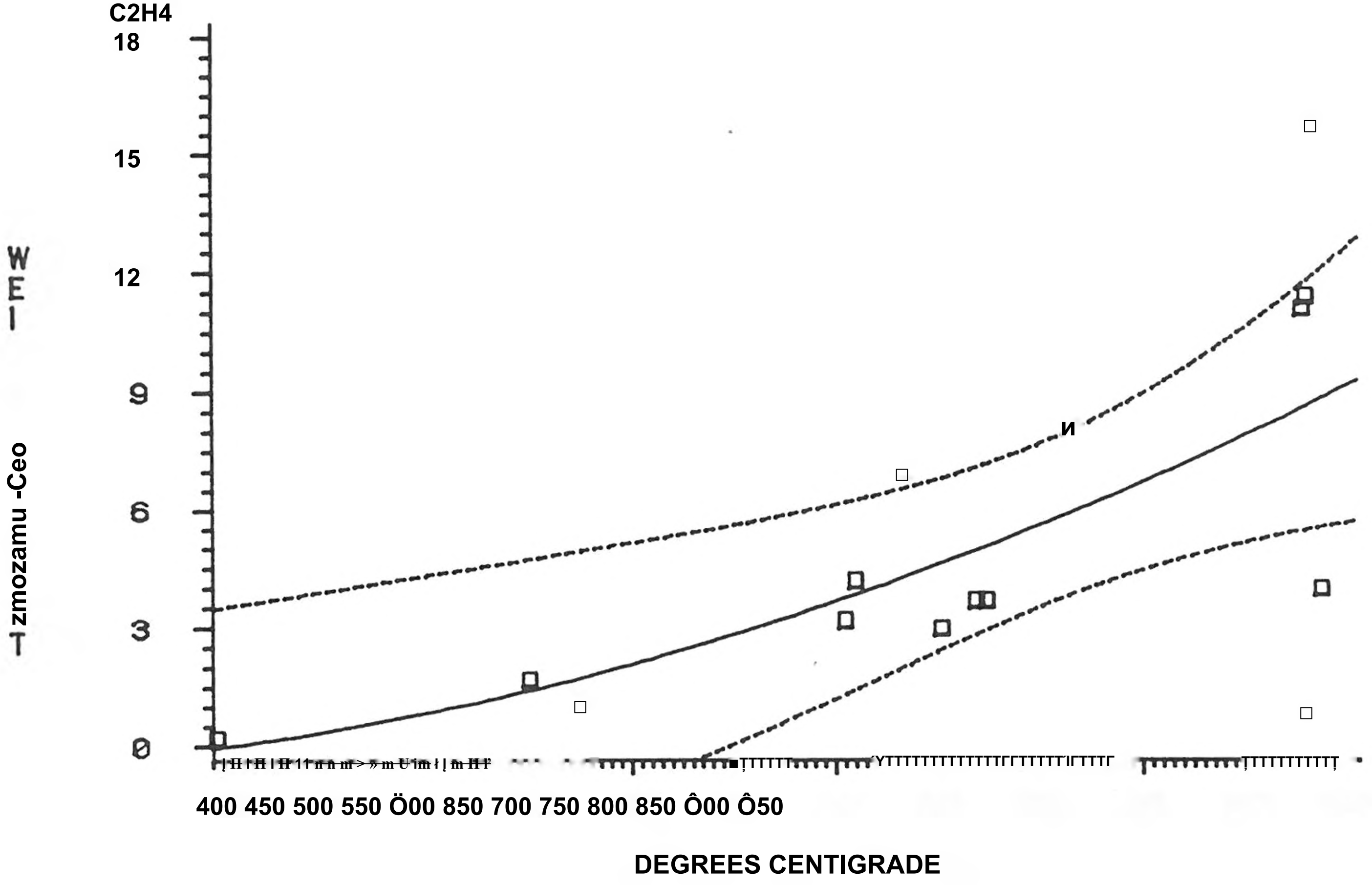
GAS COMPOSITION VS. TEMPERATURE



(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 12

GAS COMPOSITION VS. TEMPERATURE



(-------95 PERCENT CONFIDENCE LIMITS)

Figure 13

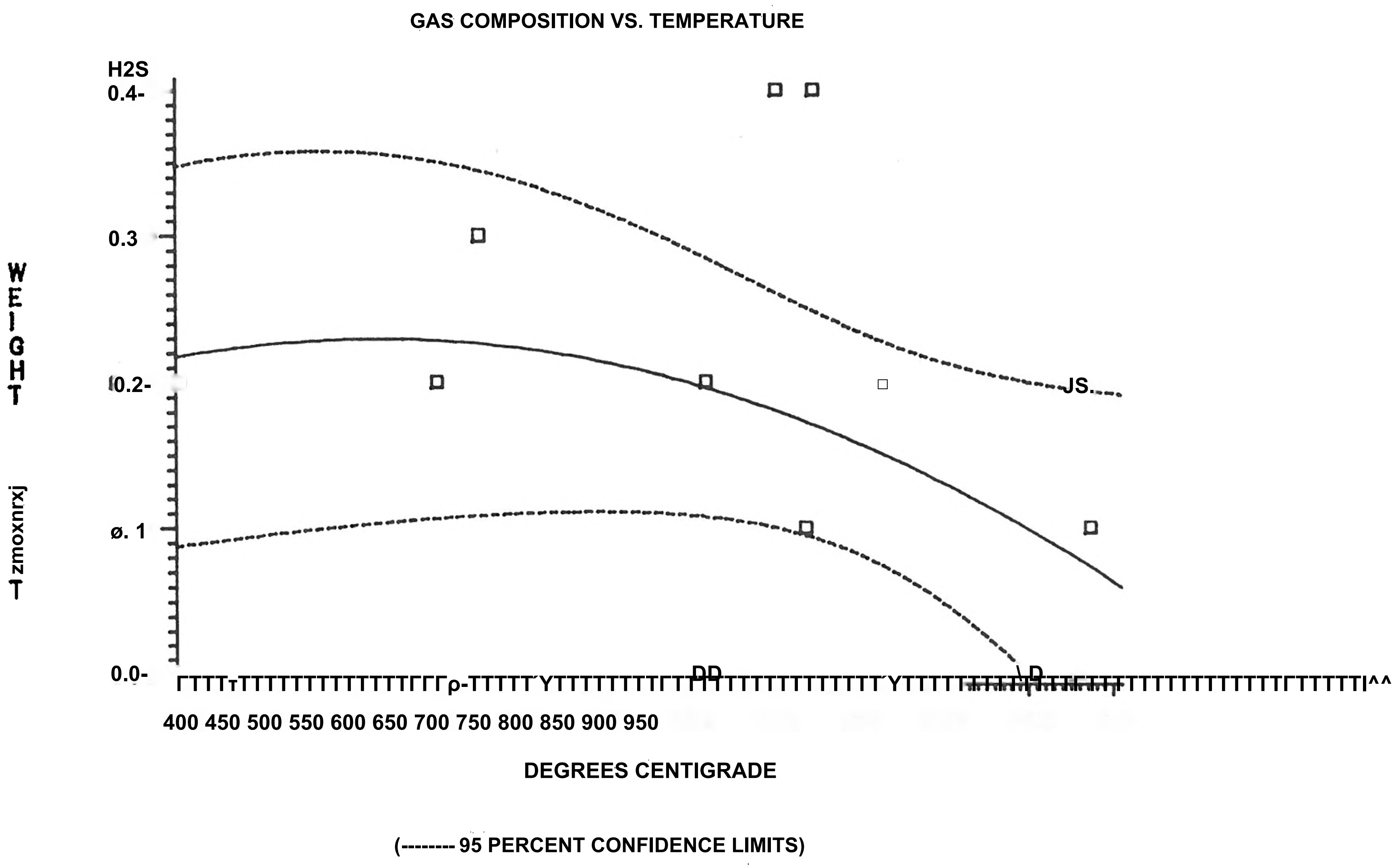

GAS COMPOSITION VS. TEMPERATURE
H2S
0.4
0.3
0.2
0.1
0.0
WEIGHT PERCENT
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 14

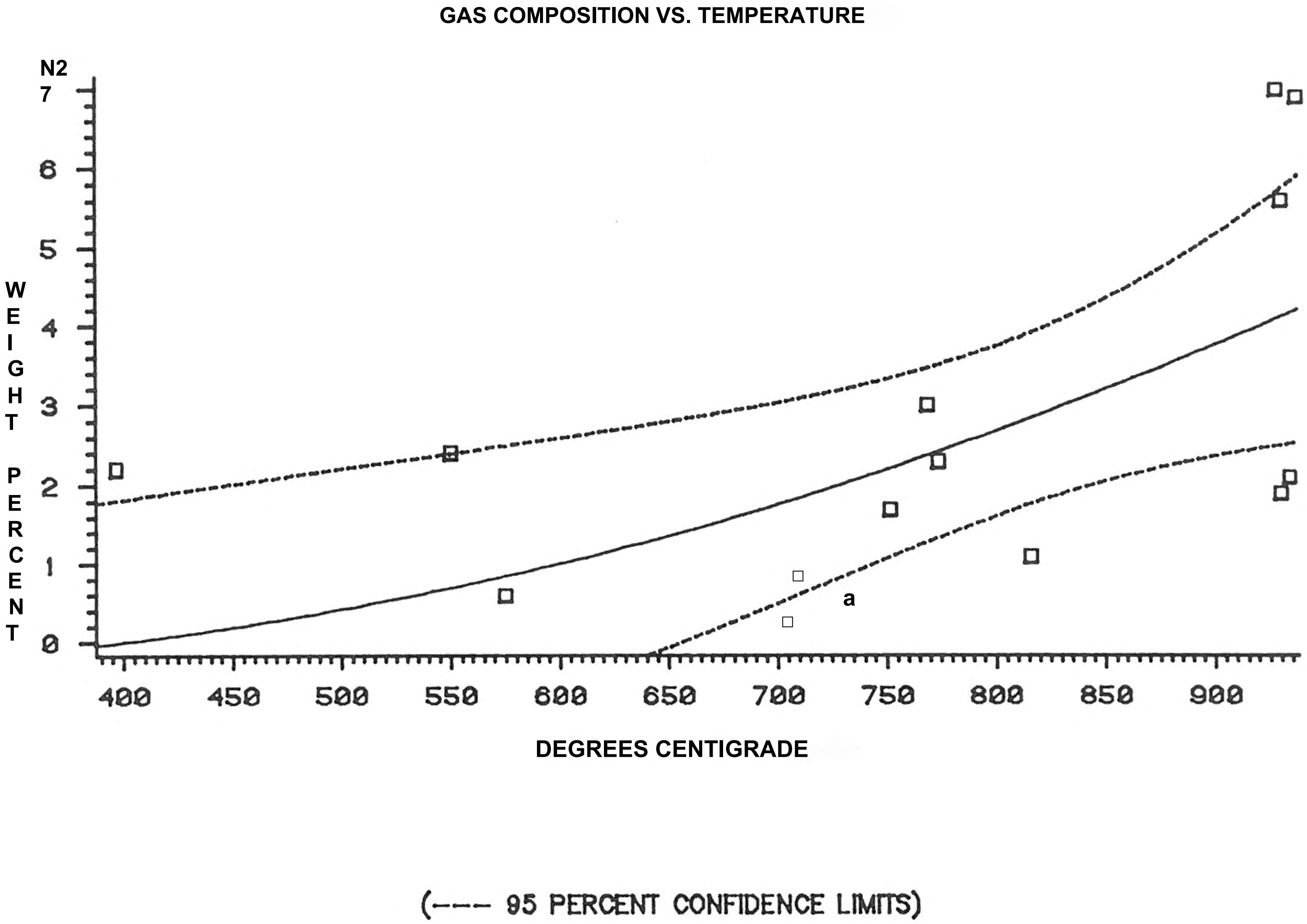
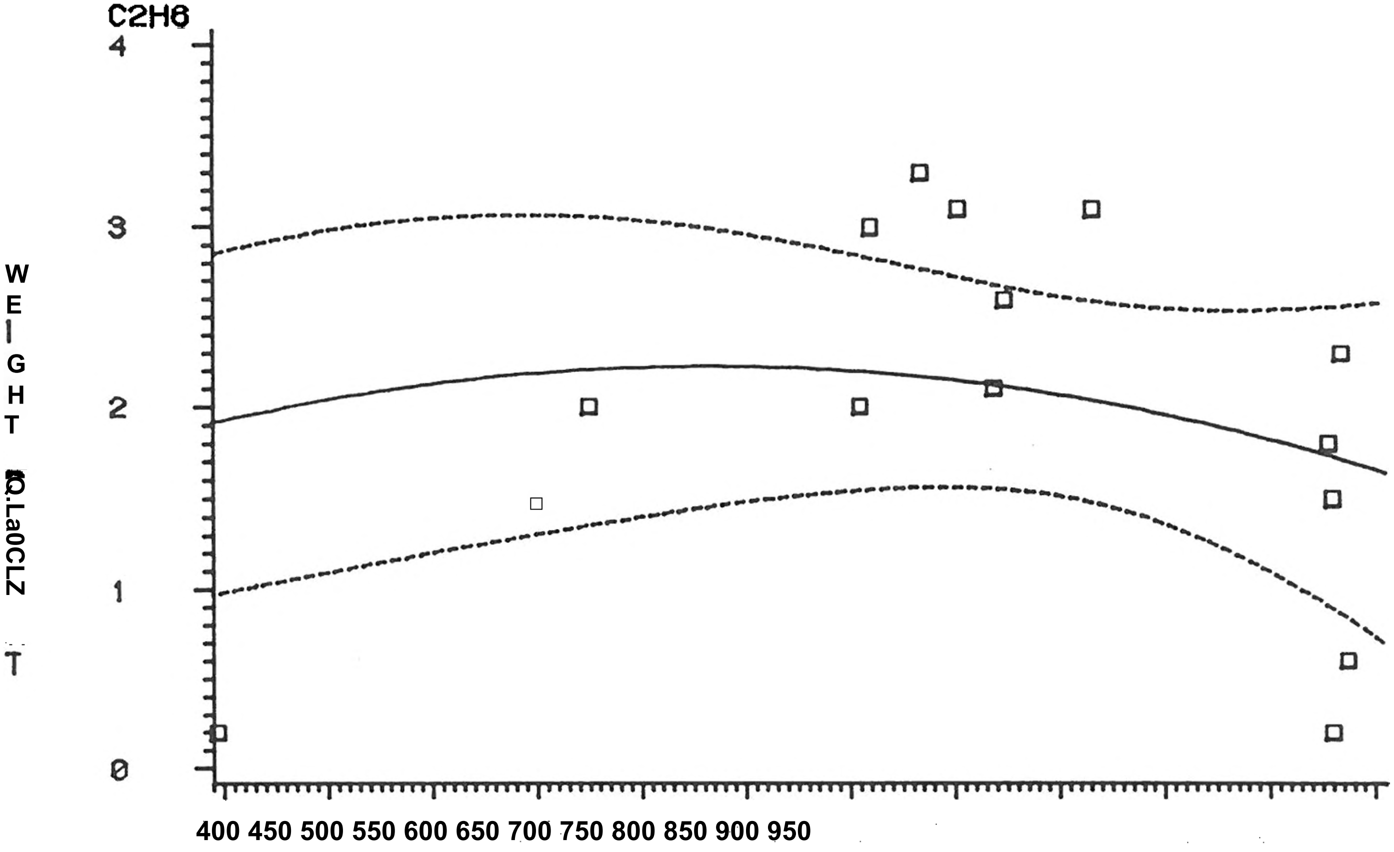

GAS COMPOSITION VS. TEMPERATURE
N2
7
6
5
4
3
2
1
0
WEIGHT PERCENT
400
450
500
550
600
650
700
750
800
850
900
a
DEGREES CENTIGRADE
(---- 95 PERCENT CONFIDENCE LIMITS)

Figure 15

GAS COMPOSITION VS. TEMPERATURE



DEGREES CENTIGRADE

(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 16

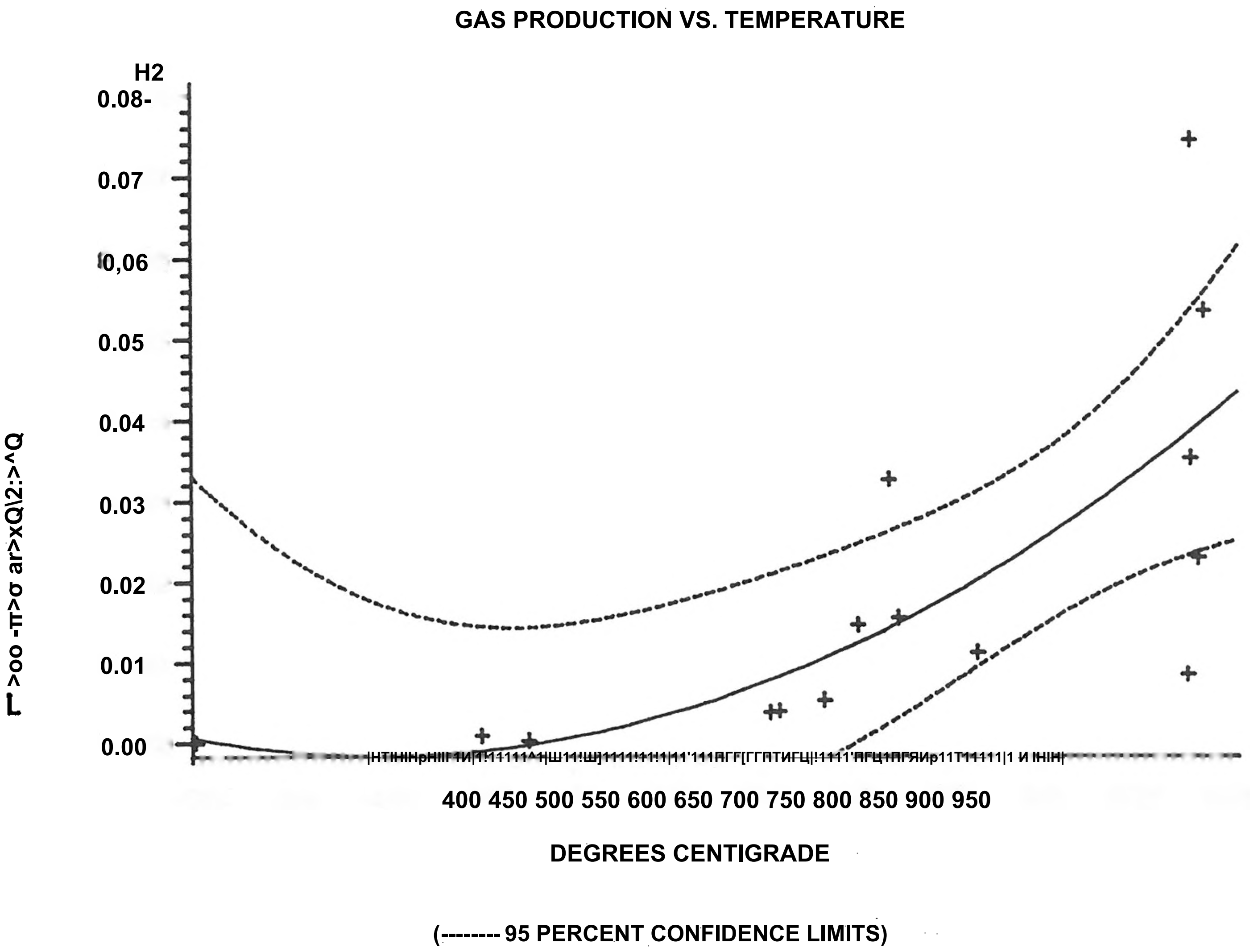

GAS PRODUCTION VS. TEMPERATURE
H2
0.08-
0.07
0,06
0.05
0.04
0.03
0.02
0.01
0.00
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 17

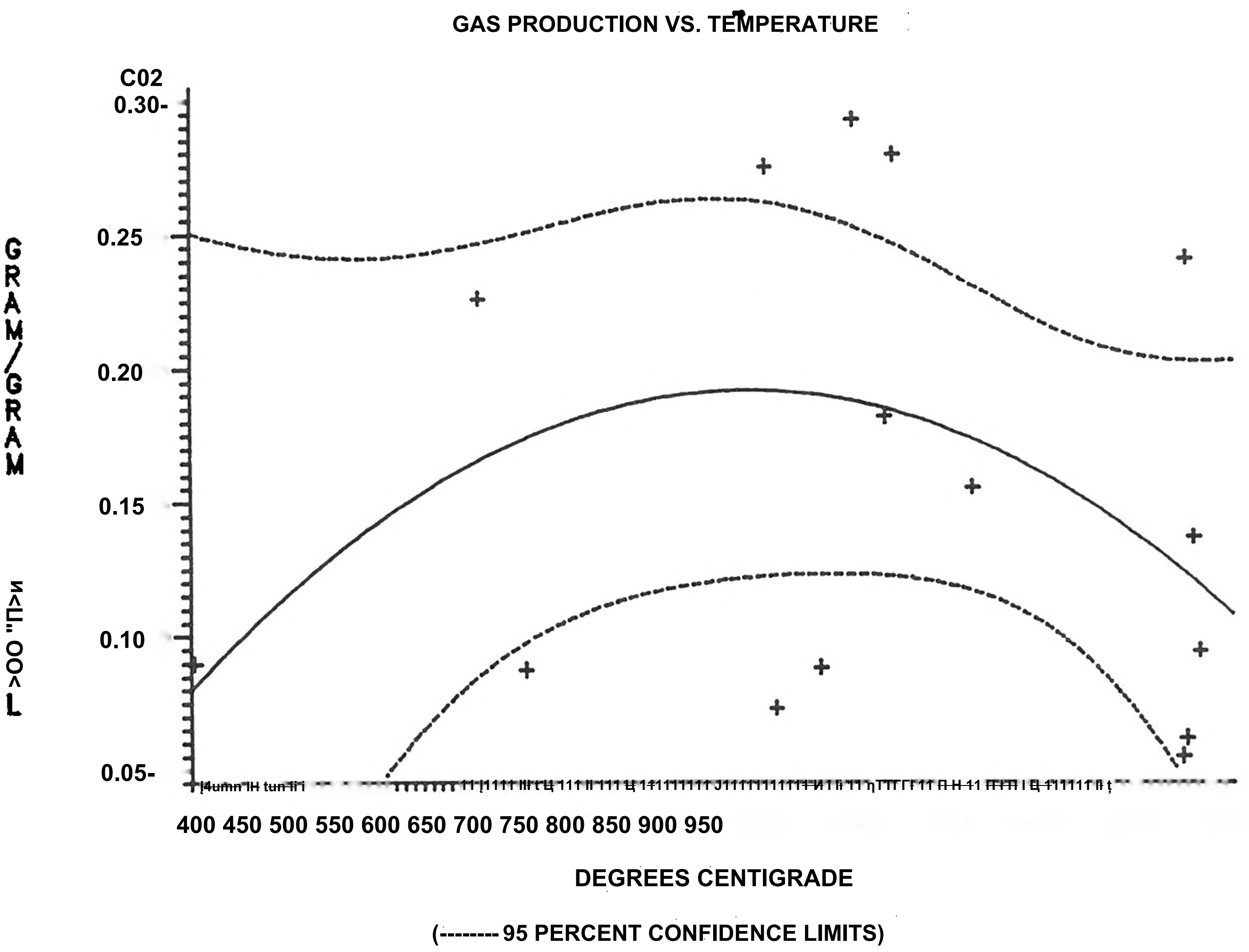

GAS PRODUCTION VS. TEMPERATURE
C02
0.30-
0.25
0.20
0.15
0.10
0.05-
GRAM/GRAM
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 18

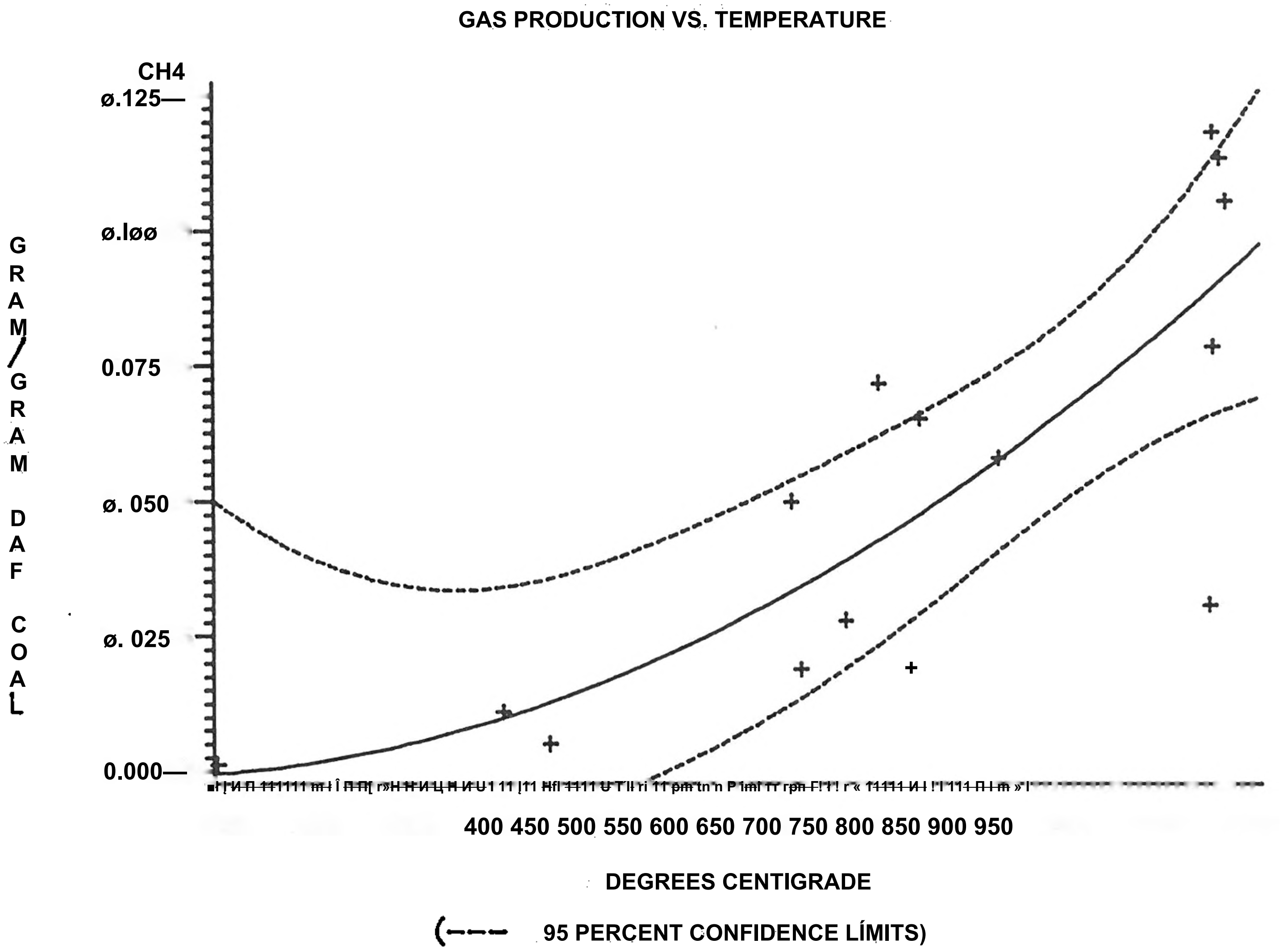

GAS PRODUCTION VS. TEMPERATURE
CH4
0.125
0.100
0.075
0.050
0.025
0.000
GRAM/GRAM DAF COAL
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(---- 95 PERCENT CONFIDENCE LIMITS)

Figure 19

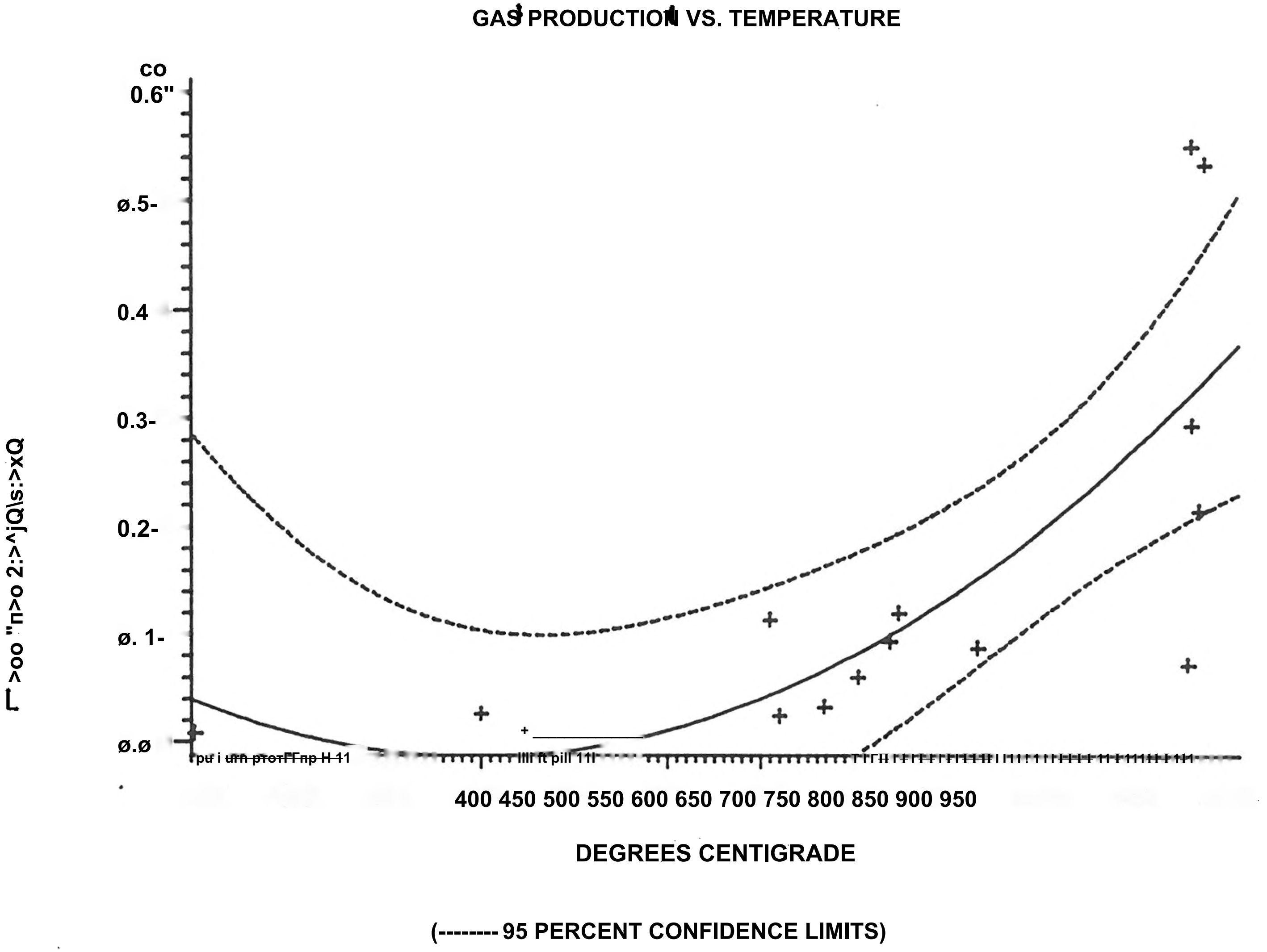

GAS PRODUCTION VS. TEMPERATURE
co
0.6"
0.5-
0.4
0.3-
0.2-
0.1-
0.0
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 20

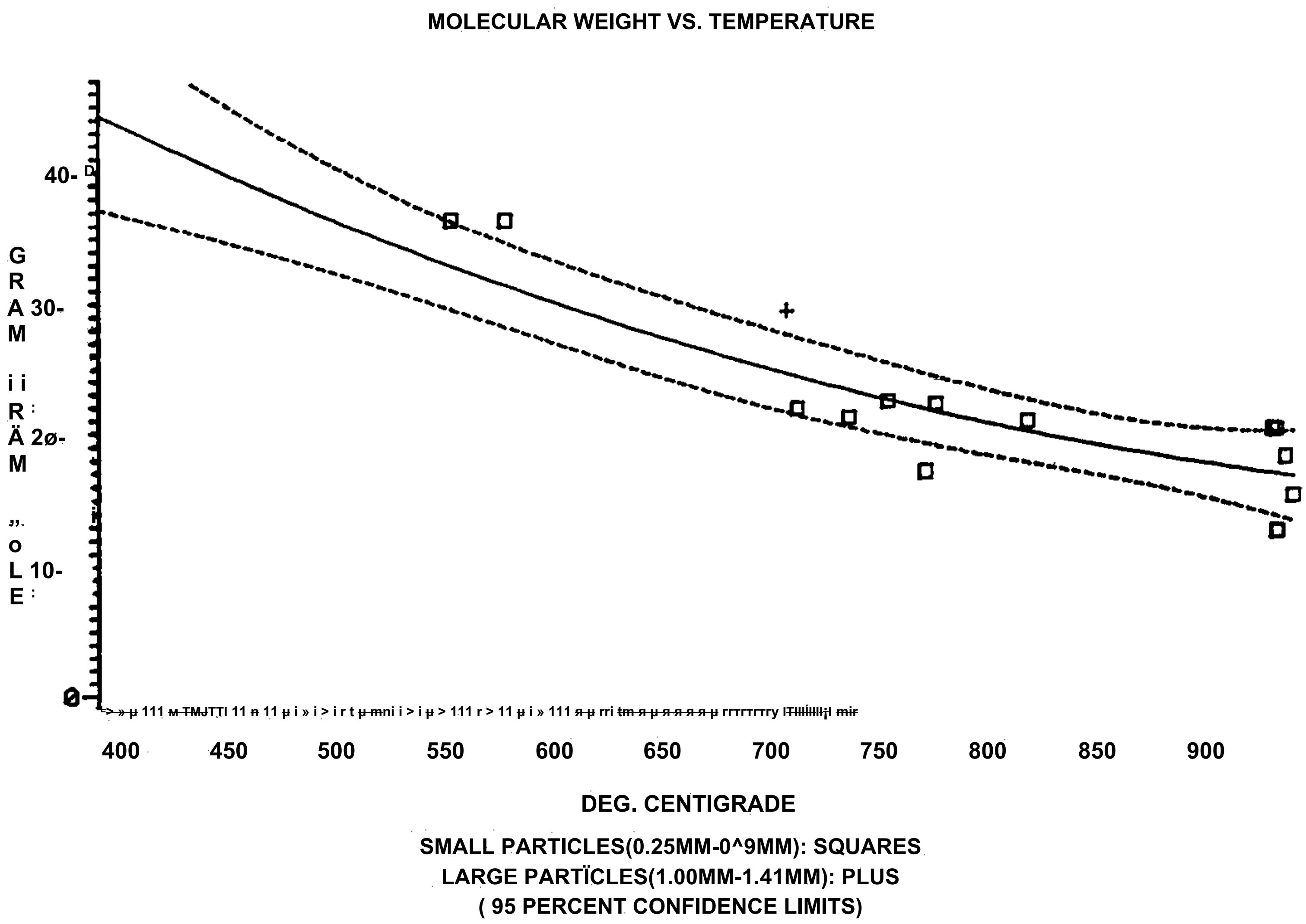
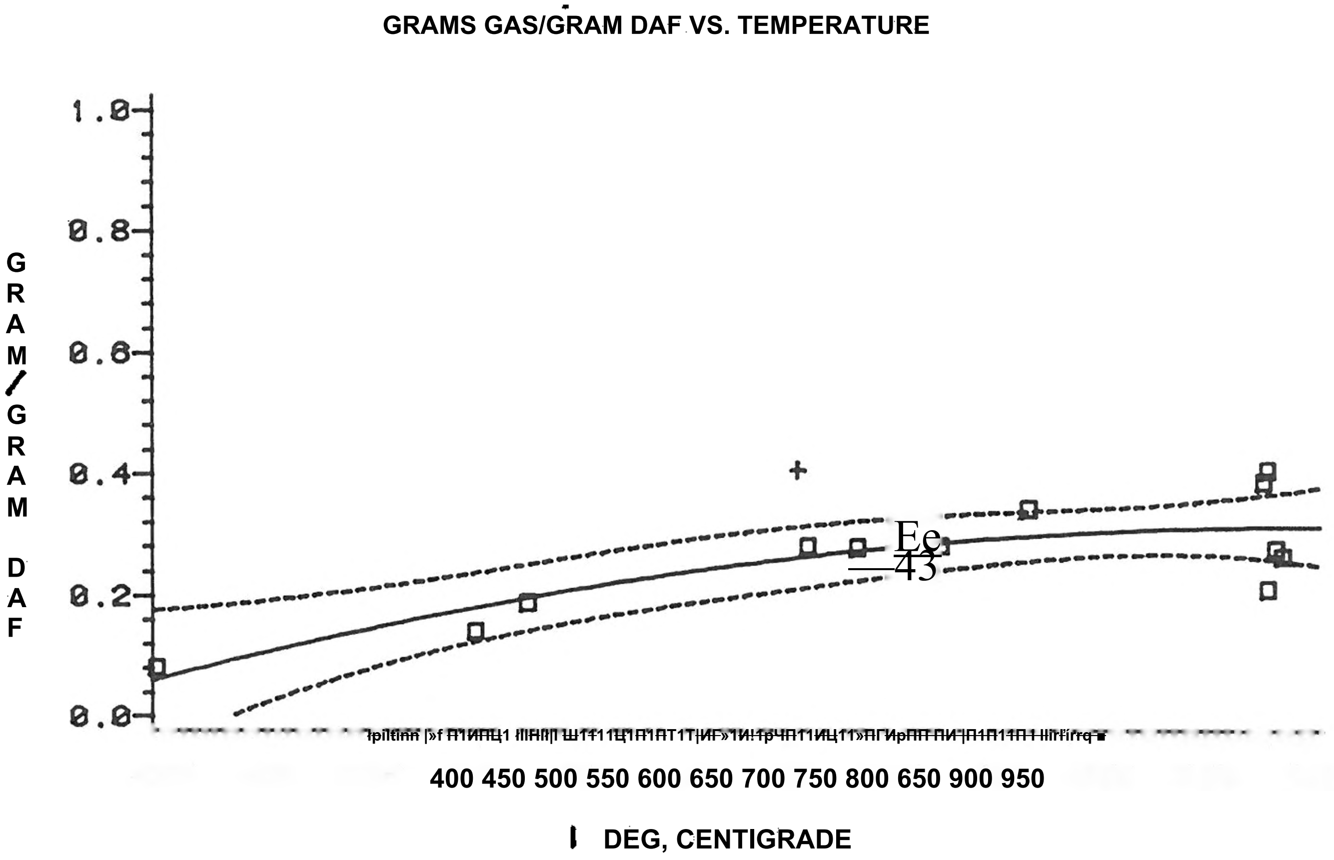
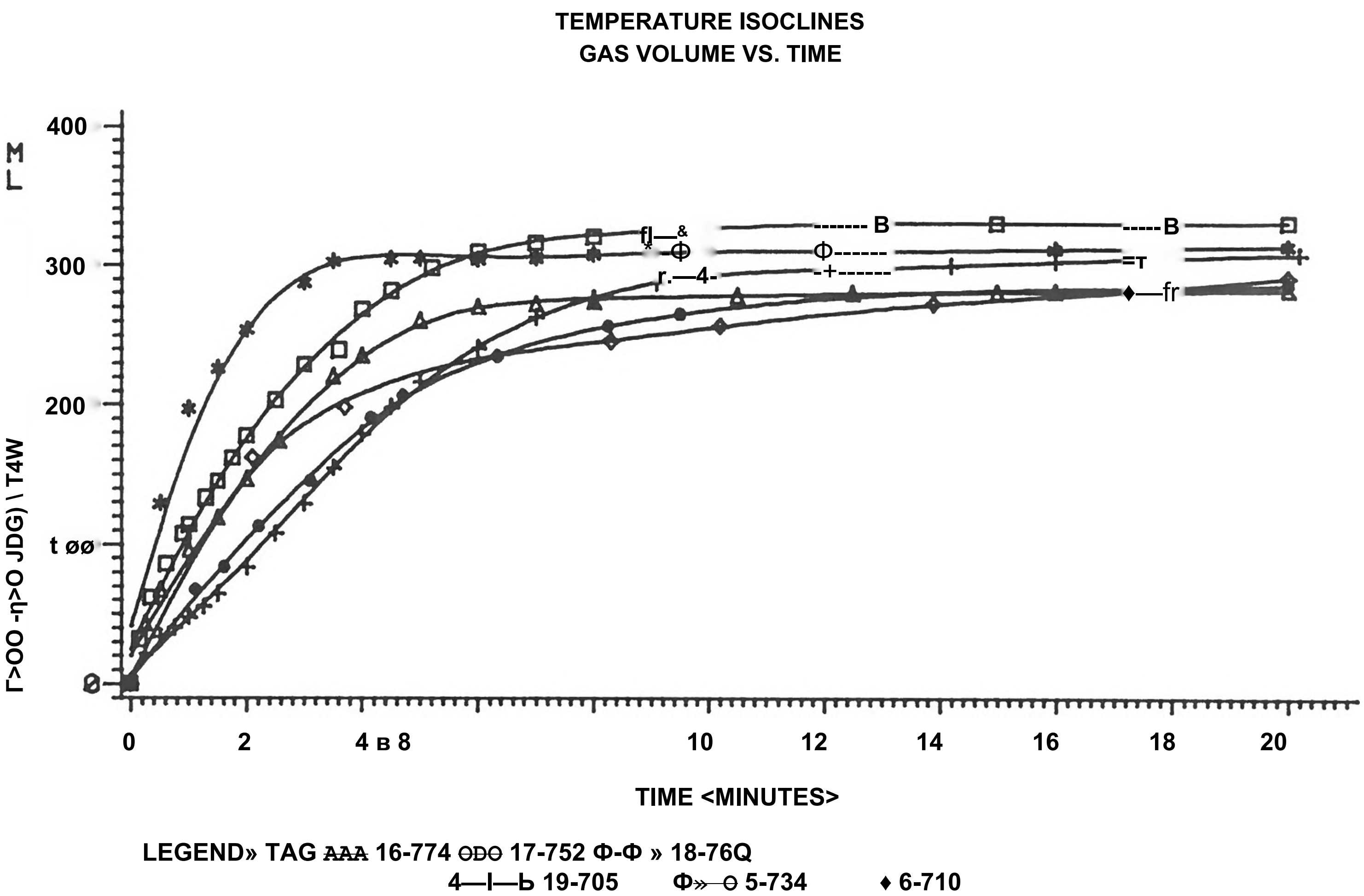

MOLECULAR WEIGHT VS. TEMPERATURE
GRAM
GRAM
MOLE
40-
30-
20-
10-
0
400
450
500
550
600
650
700
750
800
850
900
DEG. CENTIGRADE
SMALL PARTICLES(0.25MM-0^9MM): SQUARES
LARGE PARTÏCLES(1.00MM-1.41MM): PLUS
(95 PERCENT CONFIDENCE LIMITS)

Figure 21



SMALL PARTICLES(0.25MM—0.59MM): SQUARES
LARGE PARTICLES(1.00MM-1.41MM): PLUS
(95 PERCENT CONFIDENCE LIMITS)

Figure 22



TEMPERATURE ISOCLINES
GAS VOLUME VS. TIME

Figure 23

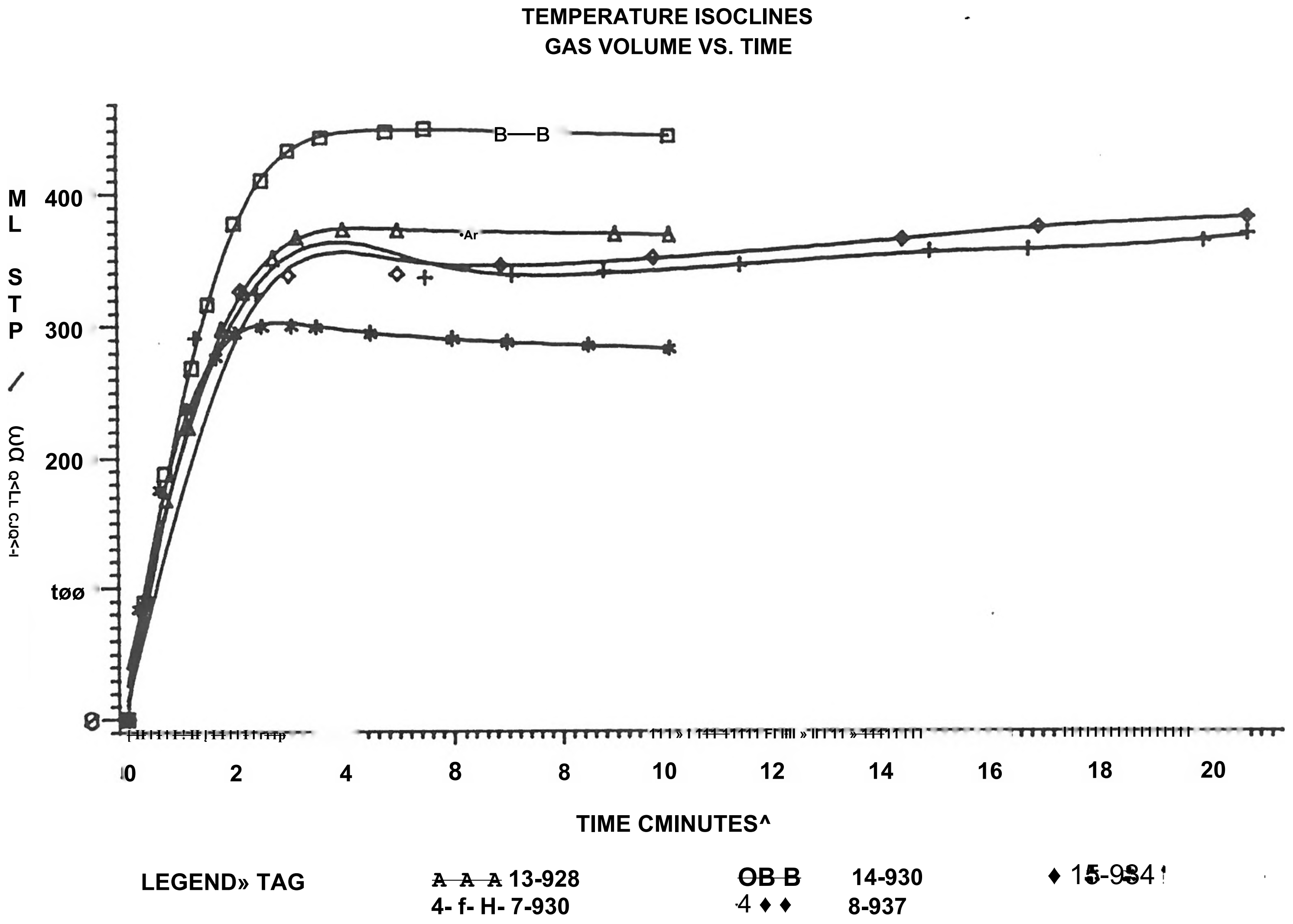

TEMPERATURE ISOCLINES
GAS VOLUME VS. TIME
ML STP
400
300
200
100
0
0
2
4
8
8
10
12
14
16
18
20
TIME (MINUTES)
LEGEND: TAG
▲ ▲ ▲ 13-928
+ + + 7-930
□ □ □ 14-930
◆ ◆ ◆ 8-937
◆ 15-934

Figure 24

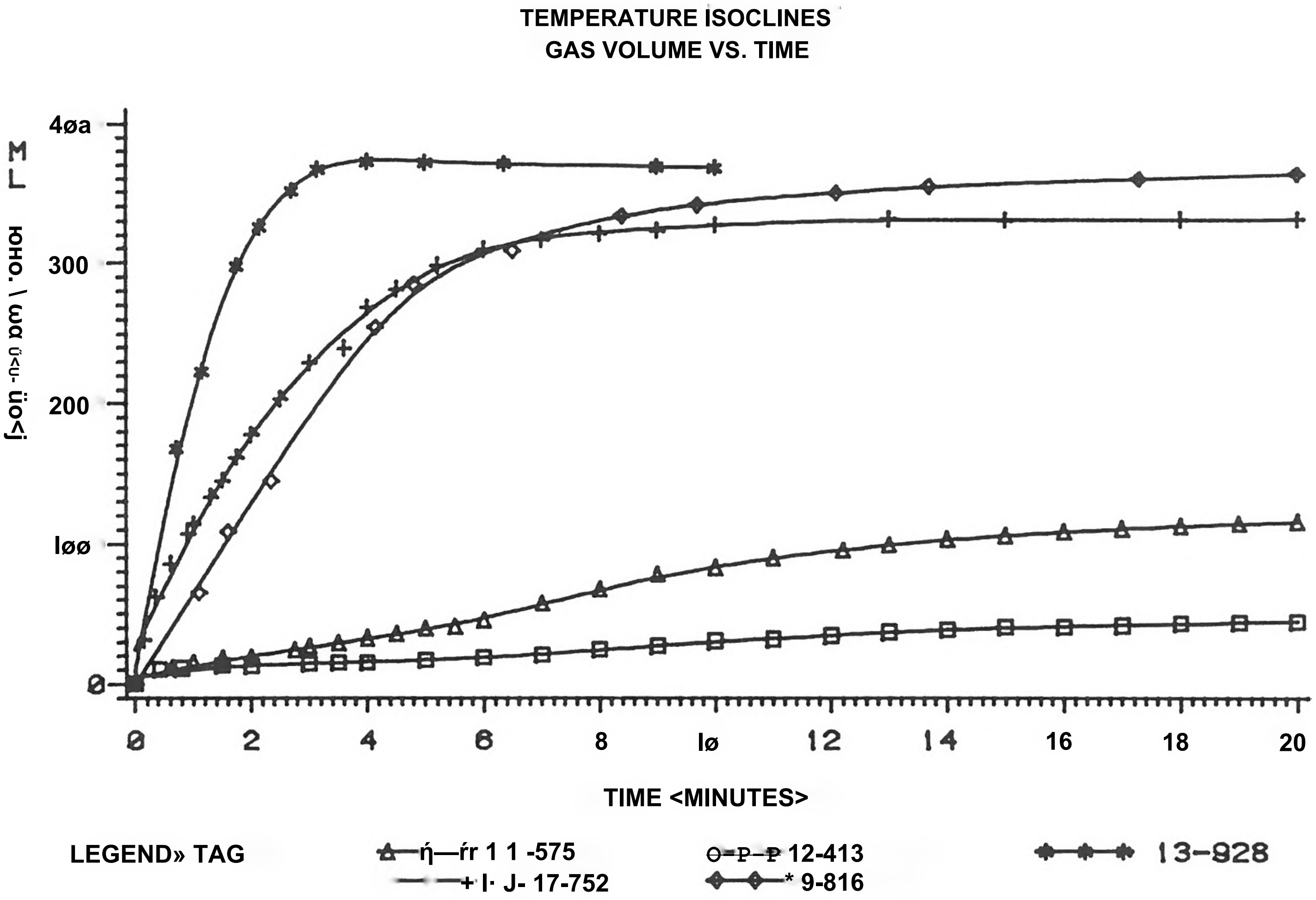

TEMPERATURE ISOCLINES
GAS VOLUME VS. TIME
ML
400
300
200
100
0
0
2
4
6
8
10
12
14
16
18
20
TIME <MINUTES>
LEGEND» TAG
△ 11-575
□ 12-413
* 13-928
+ 17-752
◆ 9-816

Figure 25

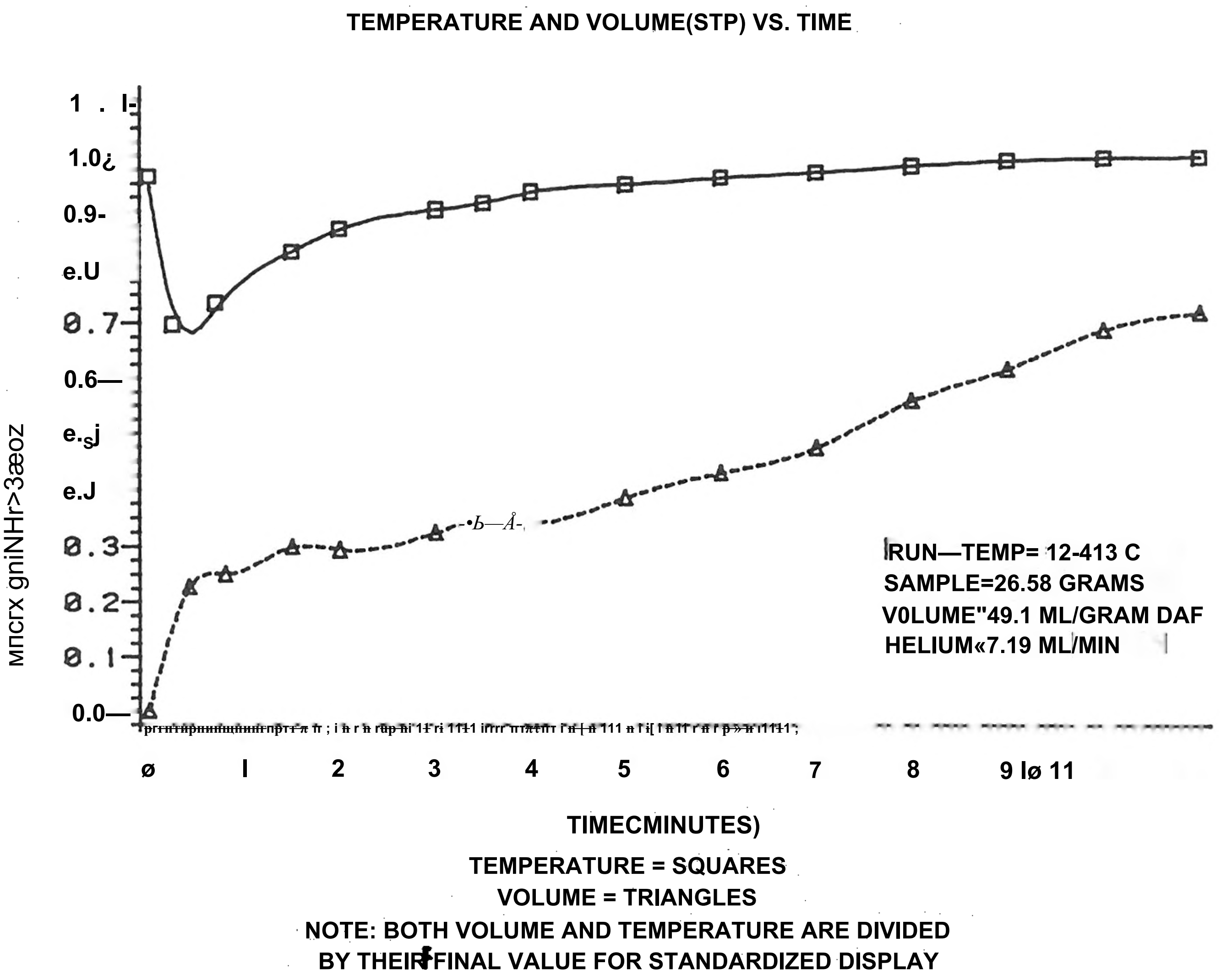
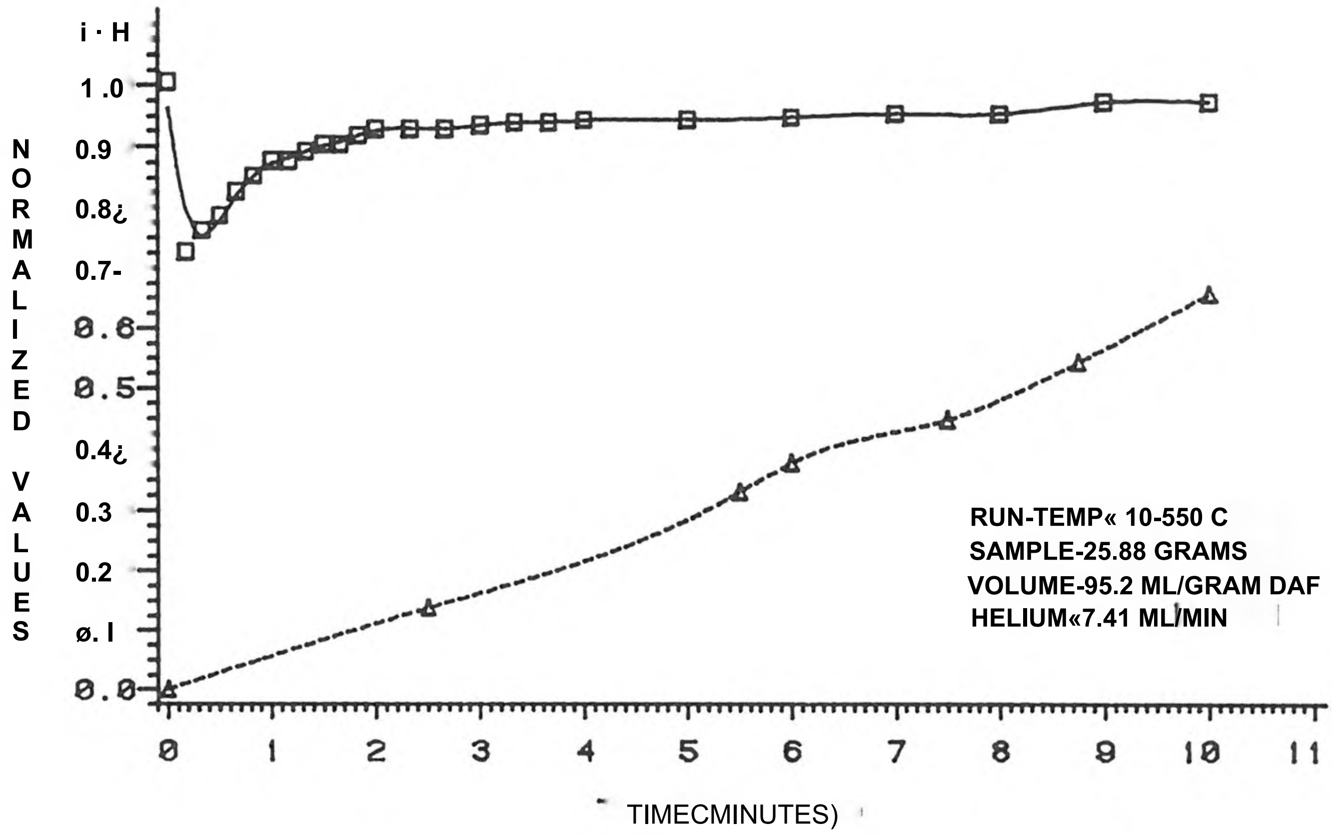

TEMPERATURE AND VOLUME(STP) VS. TIME
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
TIME(MINUTES)
RUN—TEMP= 12-413 C
SAMPLE=26.58 GRAMS
VOLUME=49.1 ML/GRAM DAF
HELIUM=7.19 ML/MIN
TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

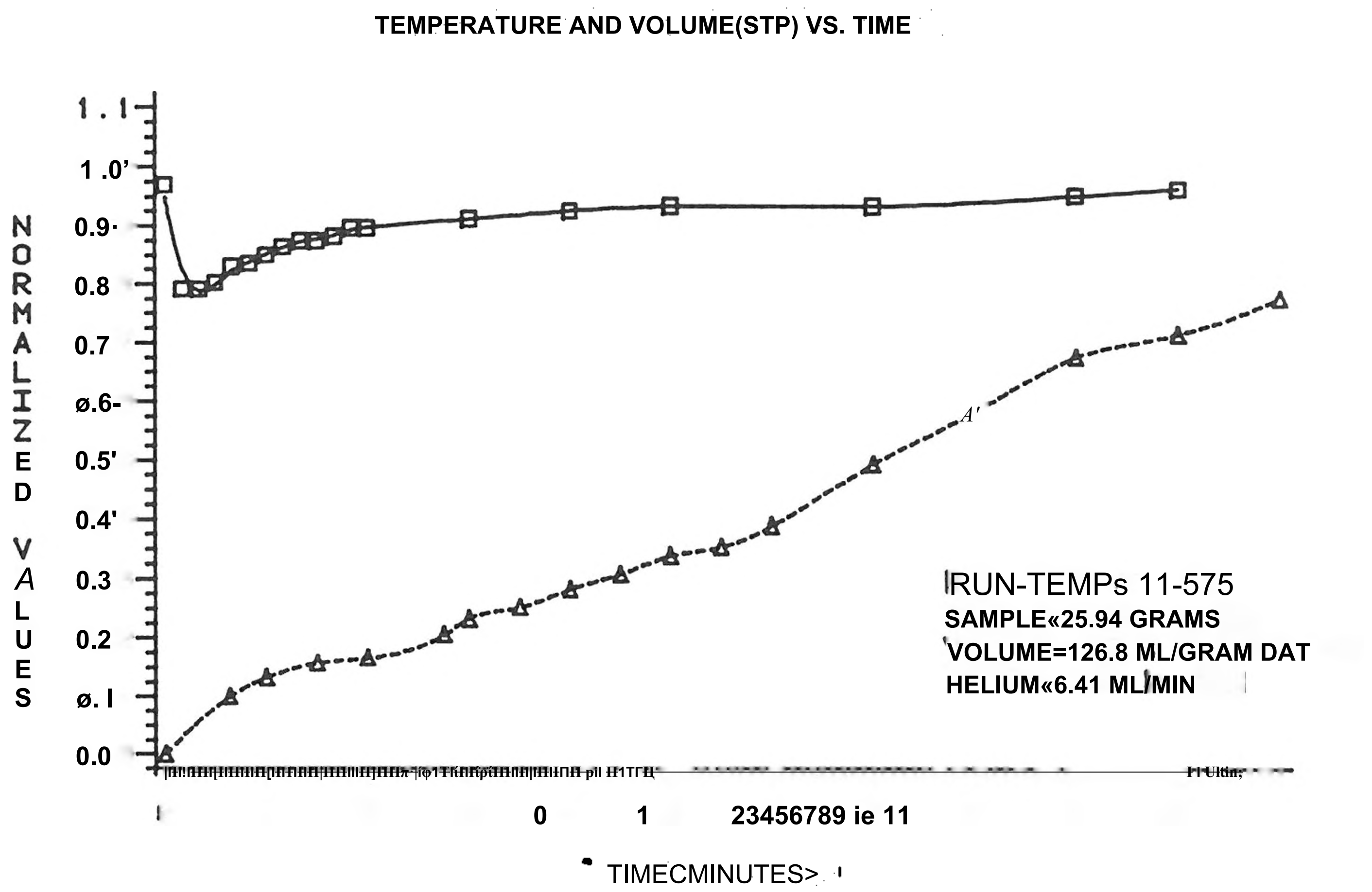
Figure 26

TEMPERATURE AND VOLUME(STP) VS. TIME



TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

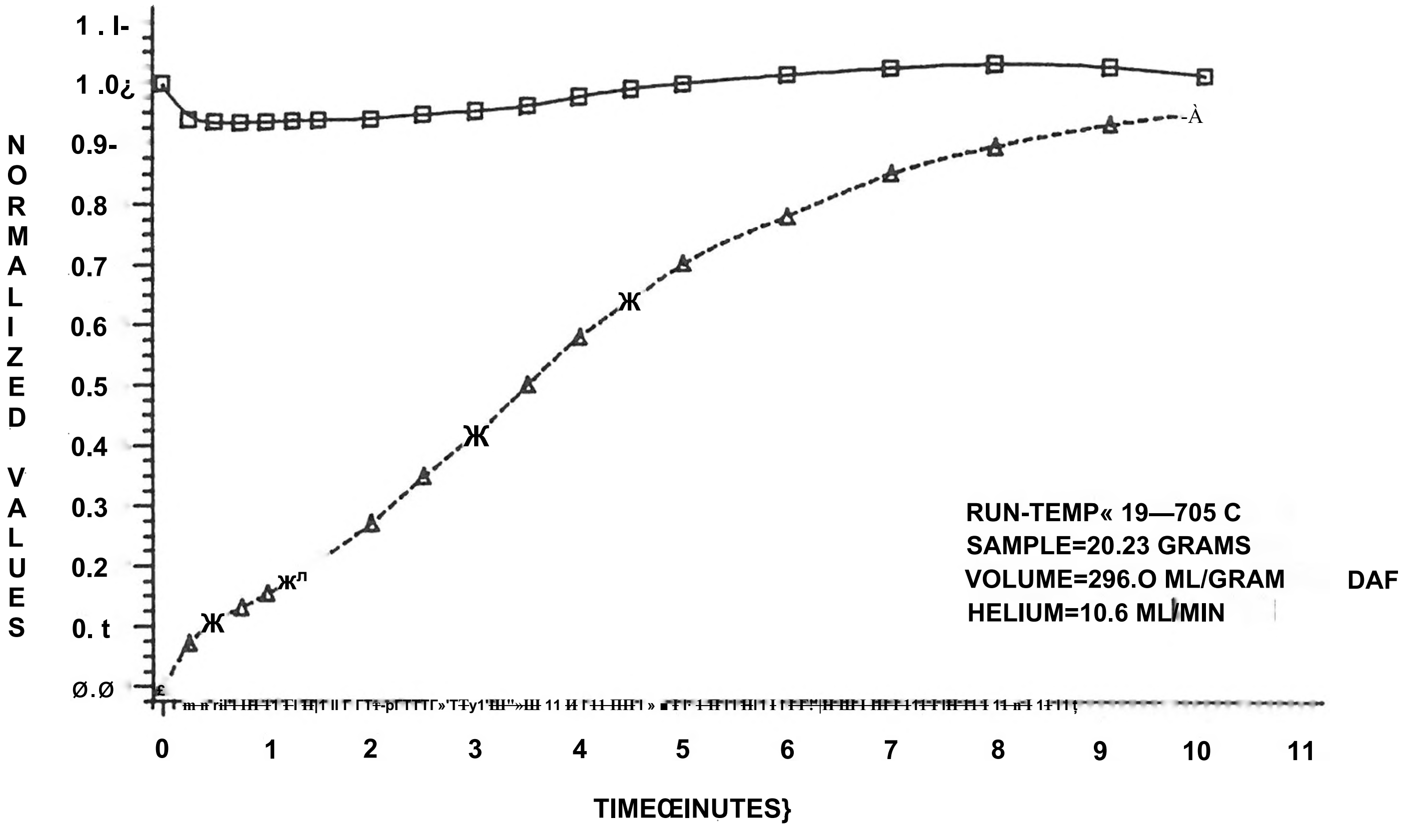
Figure 27



TEMPERATURE = SQUARES
VOLUME C TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 28

TEMPERATURE AND VOLUME(STP) VS. TIME



RUN-TEMP= 19—705 C
SAMPLE=20.23 GRAMS
VOLUME=296.0 ML/GRAM DAF
HELIUM=10.6 ML/MIN

TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 29

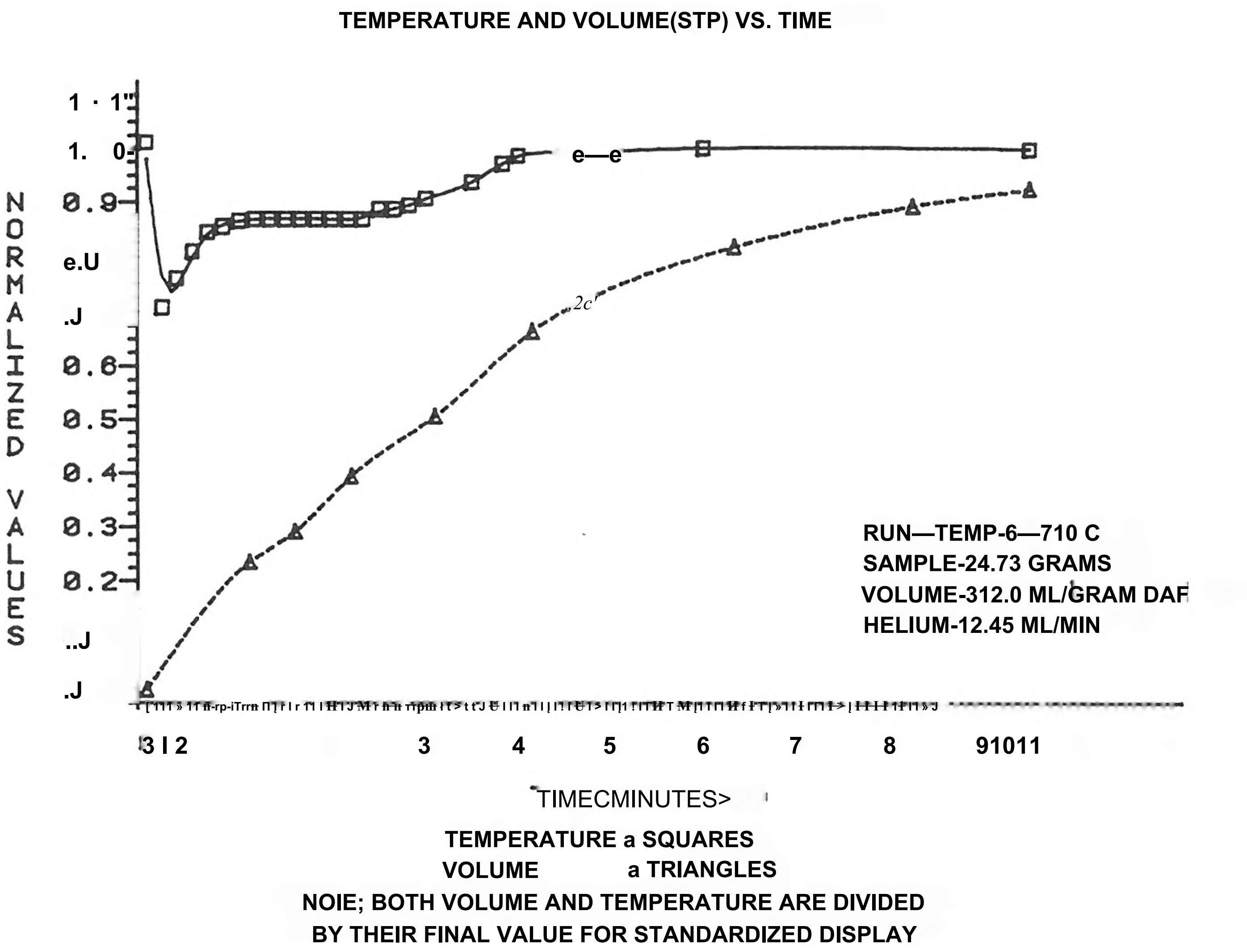

TEMPERATURE AND VOLUME(STP) VS. TIME
NORMALIZED VALUES
1 · 1
1. 0
0.9
e.U
.J
0.6
0.5
0.4
0.3
0.2
..J
.J
3 I 2
3
4
5
6
7
8
91011
TIMECMINUTES>
RUN—TEMP-6—710 C
SAMPLE-24.73 GRAMS
VOLUME-312.0 ML/GRAM DAF
HELIUM-12.45 ML/MIN
TEMPERATURE a SQUARES
VOLUME a TRIANGLES
NOIE; BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 30

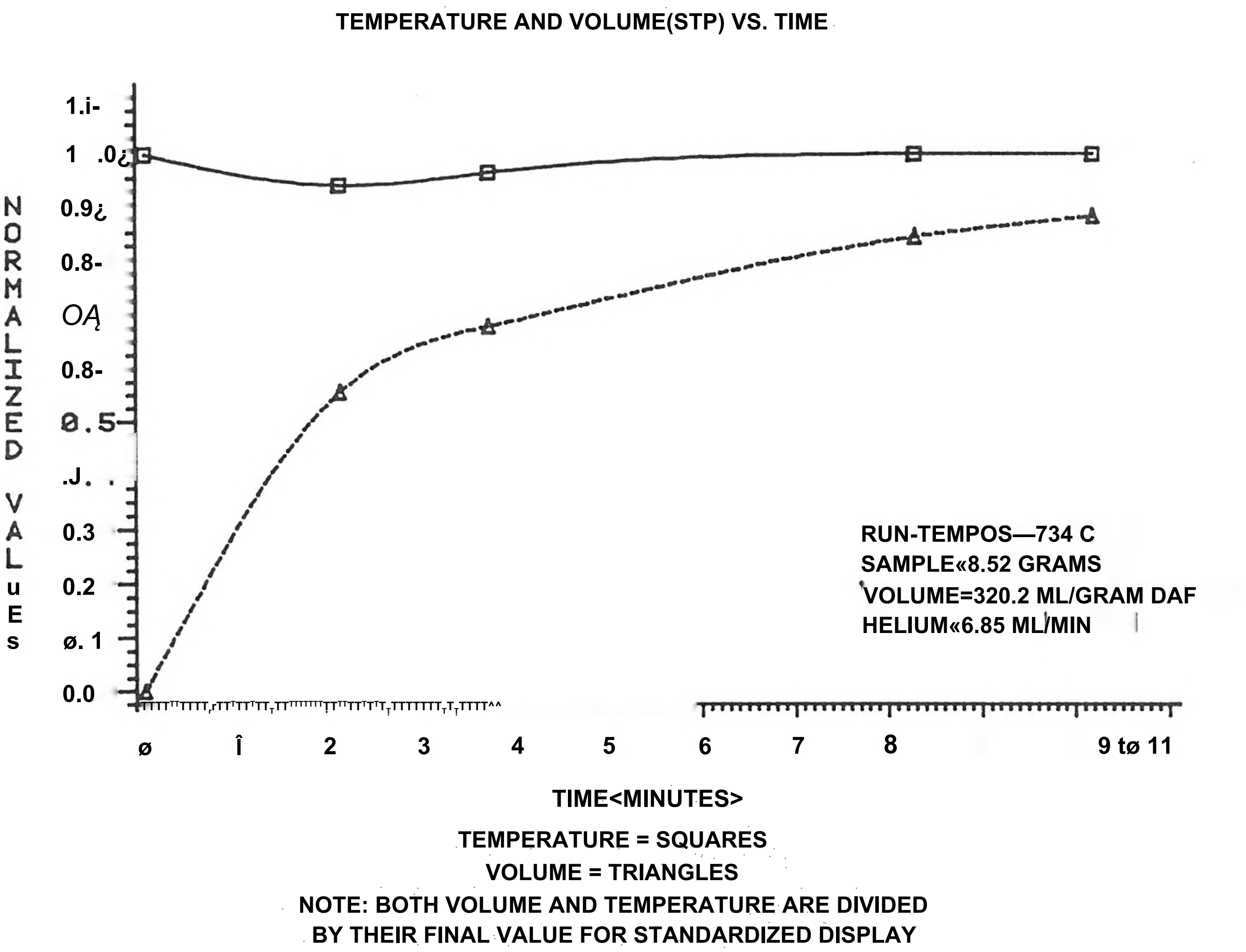
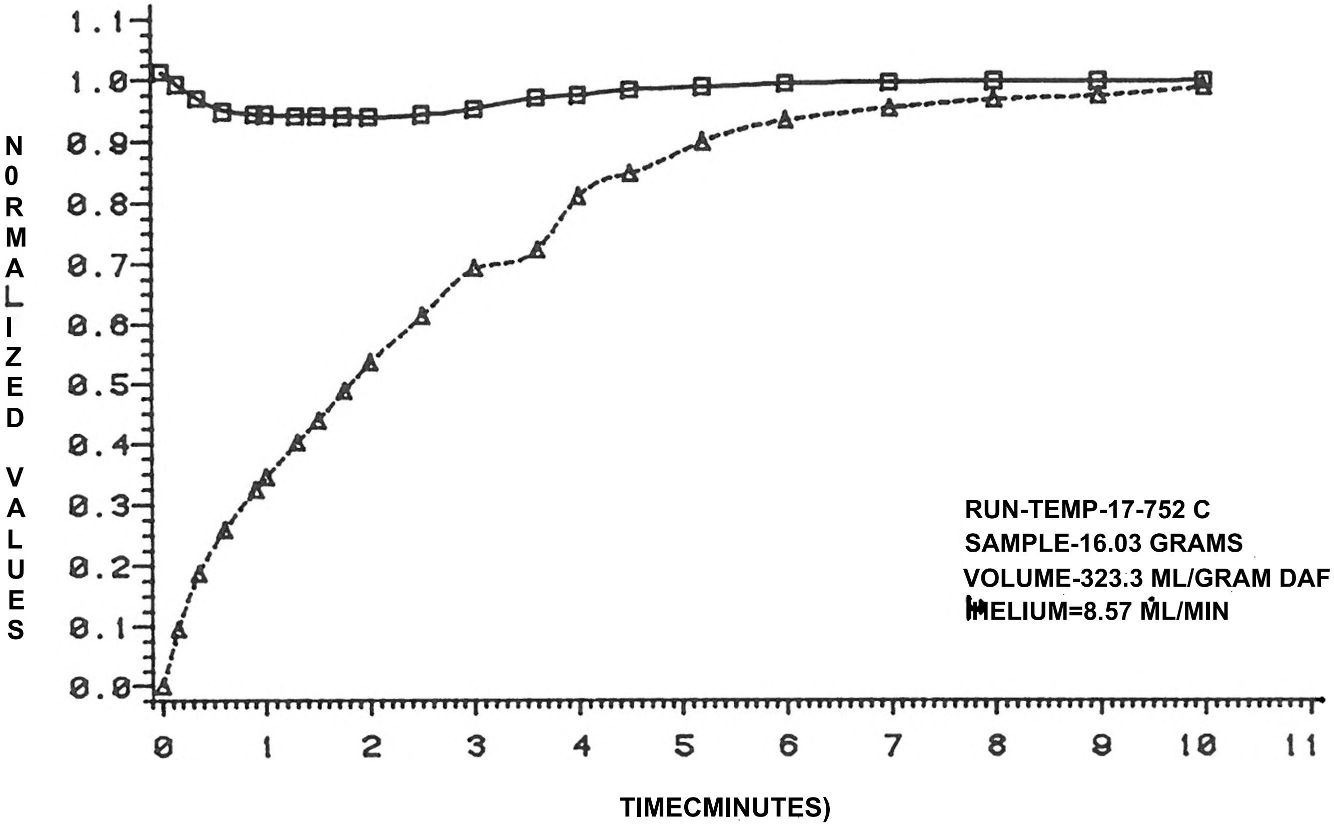

TEMPERATURE AND VOLUME(STP) VS. TIME
NORMALIZED VALUES
1.i-
1 .0¿
0.9¿
0.8-
OĄ
0.8-
0.5
.J.
0.3
0.2
0.1
0.0
0
Î
2
3
4
5
6
7
8
9 t0 11
TIME<MINUTES>
RUN-TEMPOS—734 C
SAMPLE«8.52 GRAMS
VOLUME=320.2 ML/GRAM DAF
HELIUM«6.85 ML/MIN
TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 31

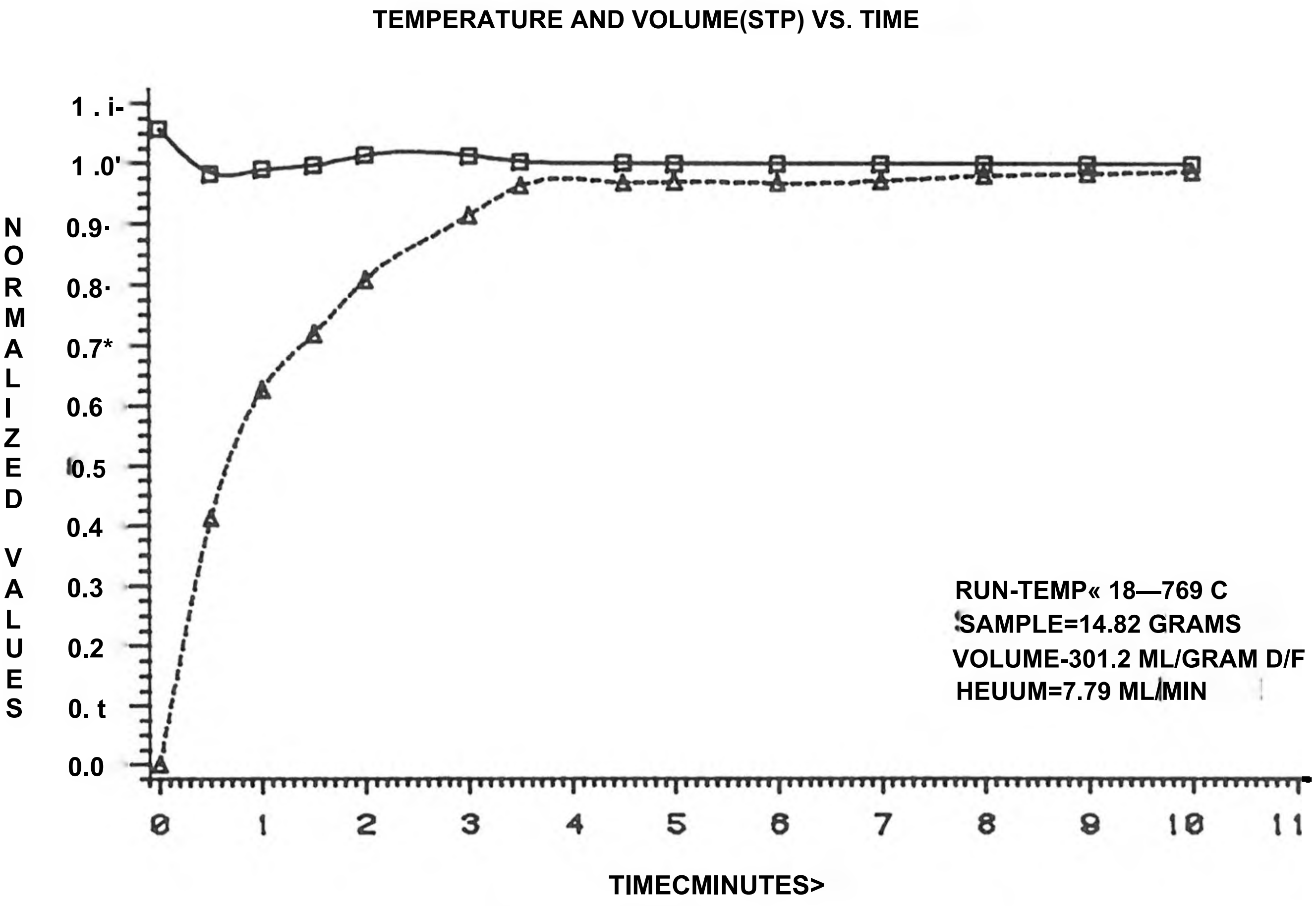
TEMPERATURE AND VOLUME(STP) VS. ЯME



RUN-TEMP-17-752 C
SAMPLE-16.03 GRAMS
VOLUME-323.3 ML/GRAM DAF
HELIUM=8.57 ML/MIN

TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 32



TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOIE: BOTH VOLUME AND TEMPERATURE ARE DMDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 33

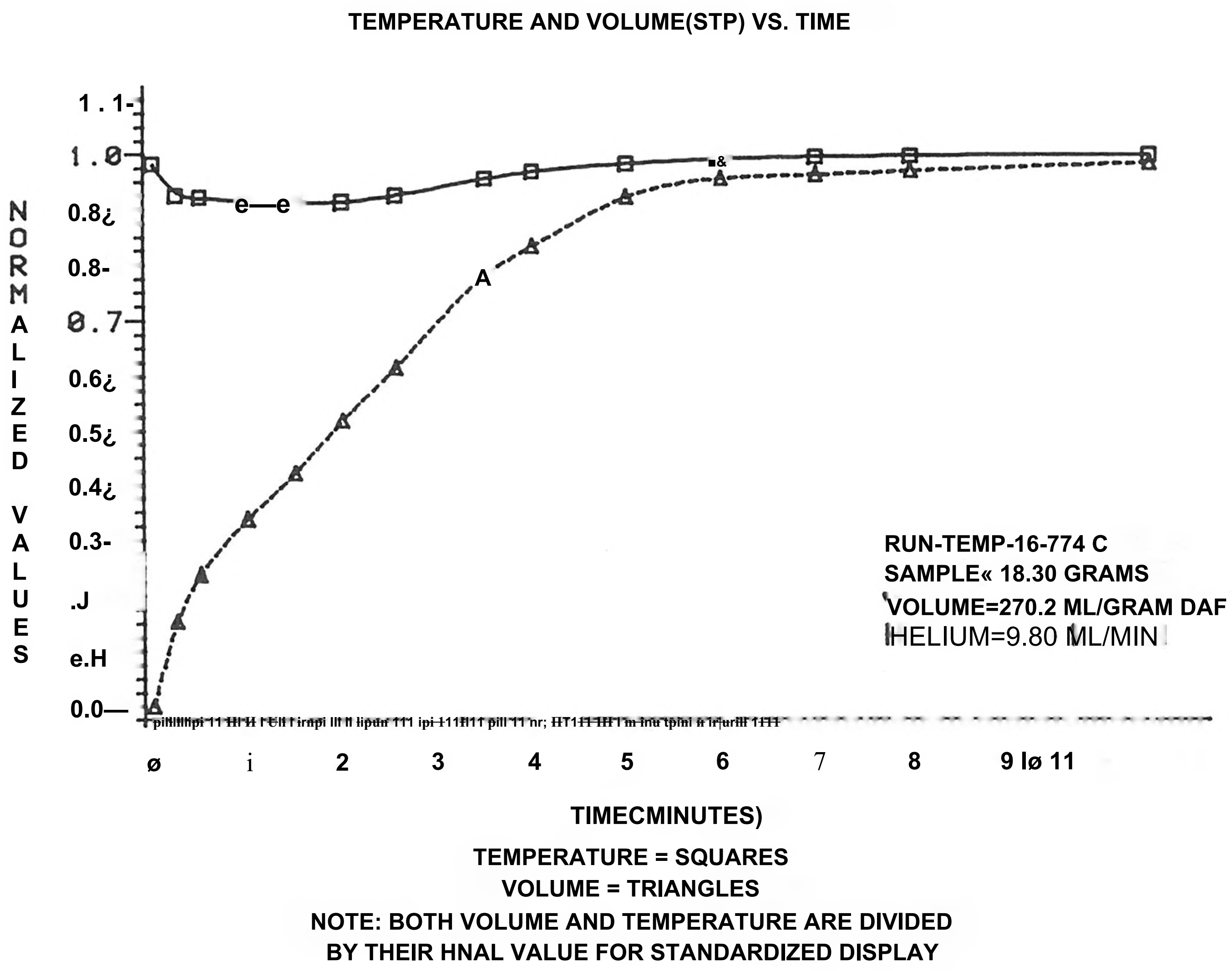
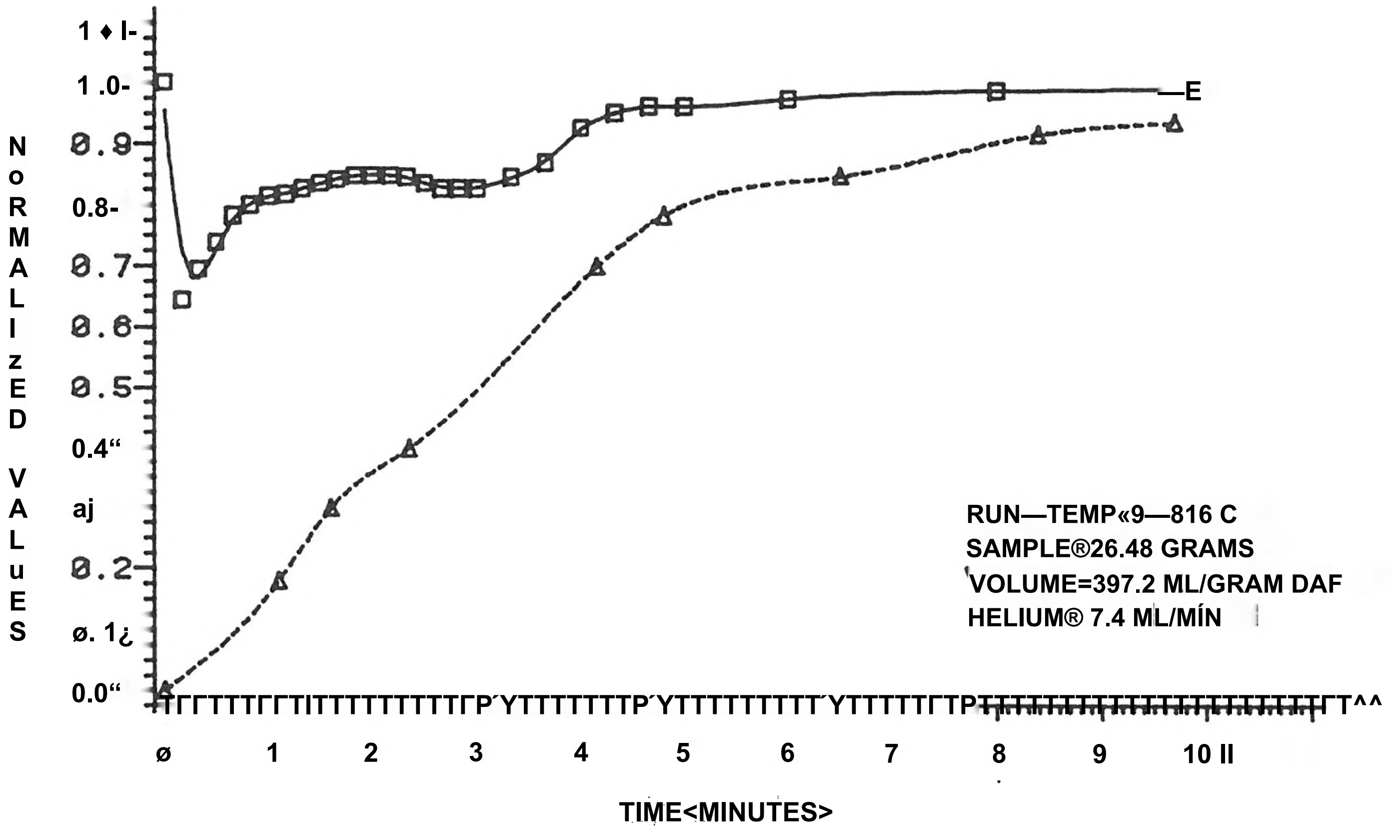

TEMPERATURE AND VOLUME(STP) VS. TIME
NORMALIZED VALUES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
TIME(MINUTES)
RUN-TEMP-16-774 C
SAMPLE= 18.30 GRAMS
VOLUME=270.2 ML/GRAM DAF
HELIUM=9.80 ML/MIN
TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 34

TEMPERATURE AND VOLUME(STP) VS. TIME



TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 35

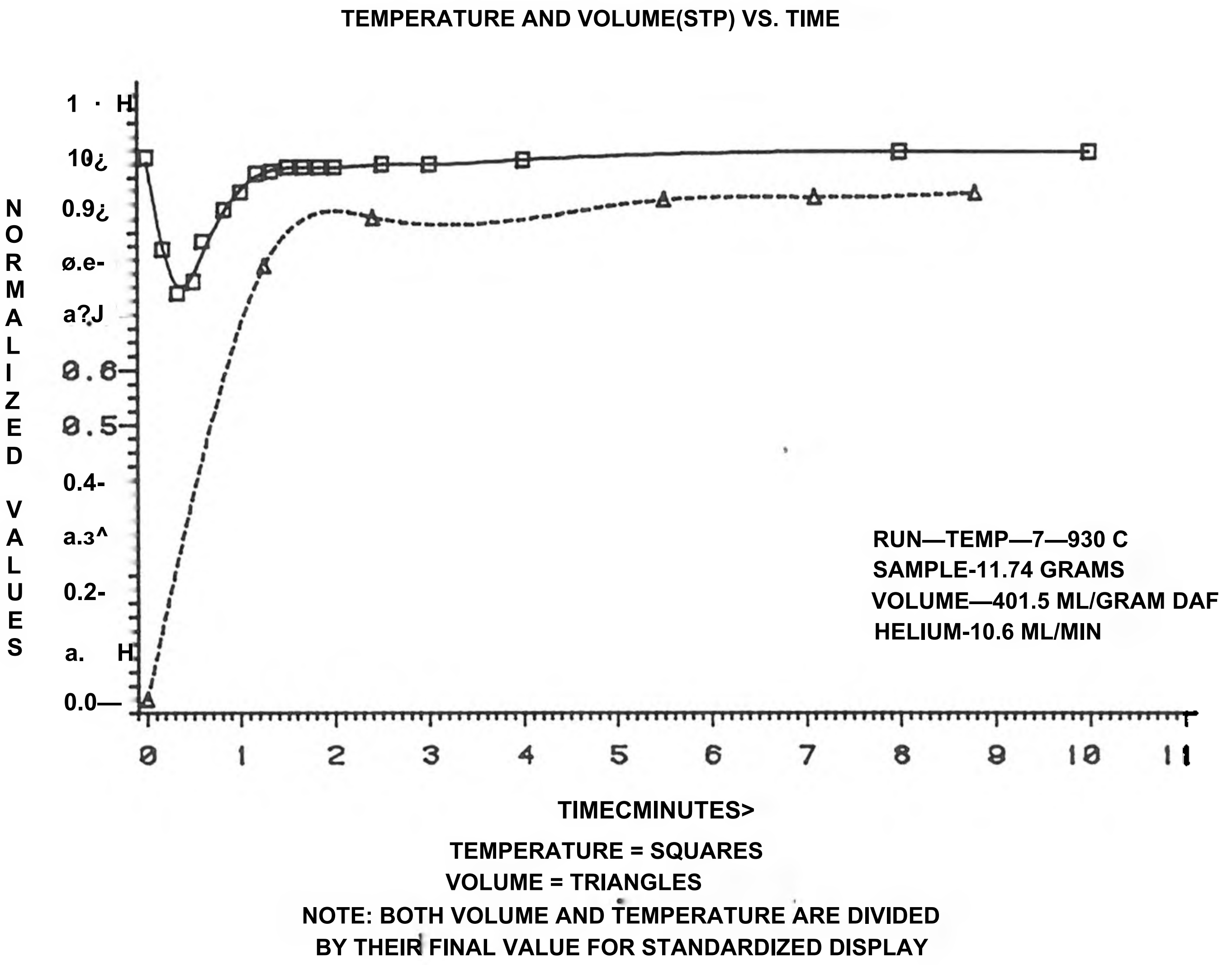

TEMPERATURE AND VOLUME(STP) VS. TIME
NORMALIZED VALUES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
TIME(MINUTES)
RUN—TEMP—7—930 C
SAMPLE-11.74 GRAMS
VOLUME—401.5 ML/GRAM DAF
HELIUM-10.6 ML/MIN
TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 36

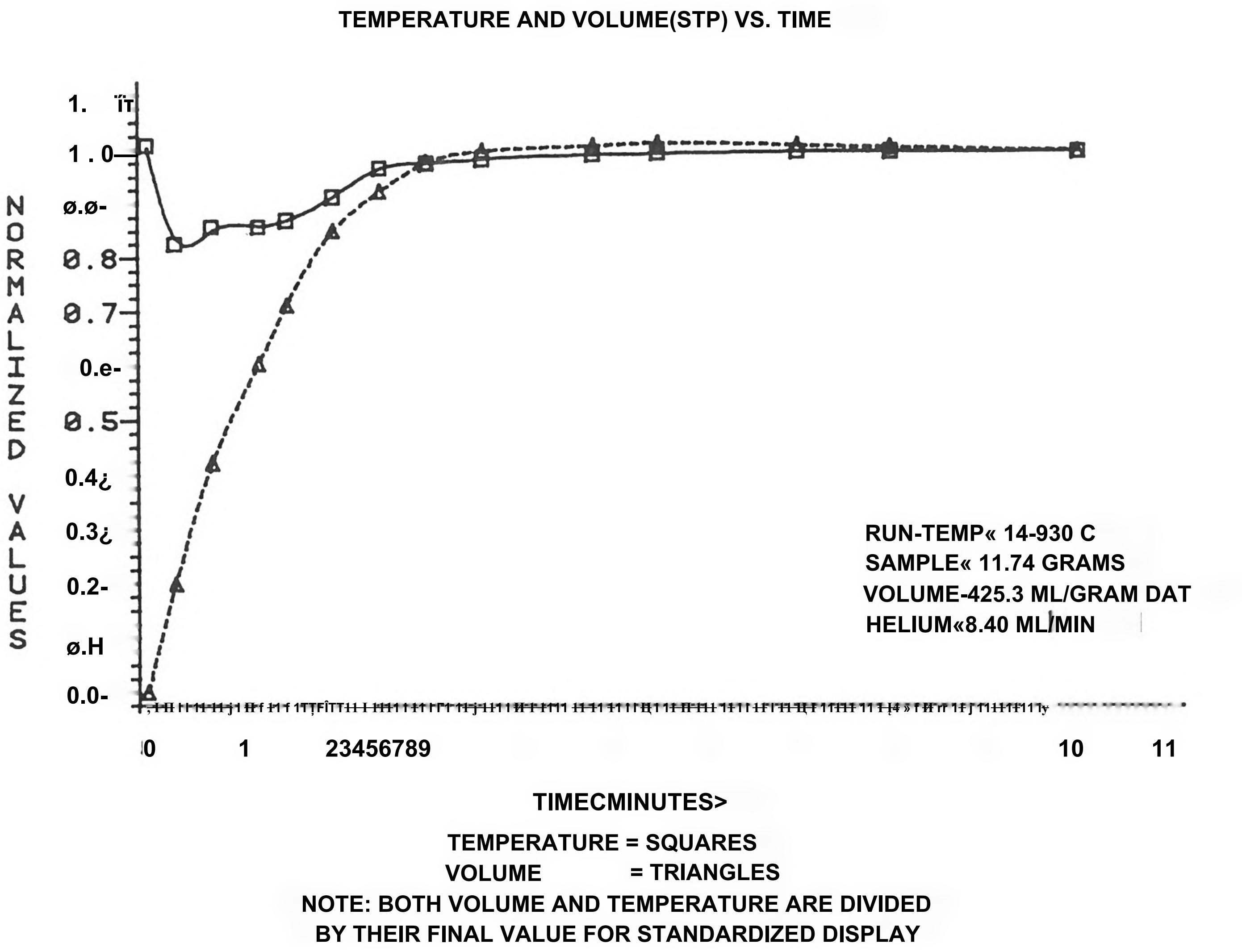
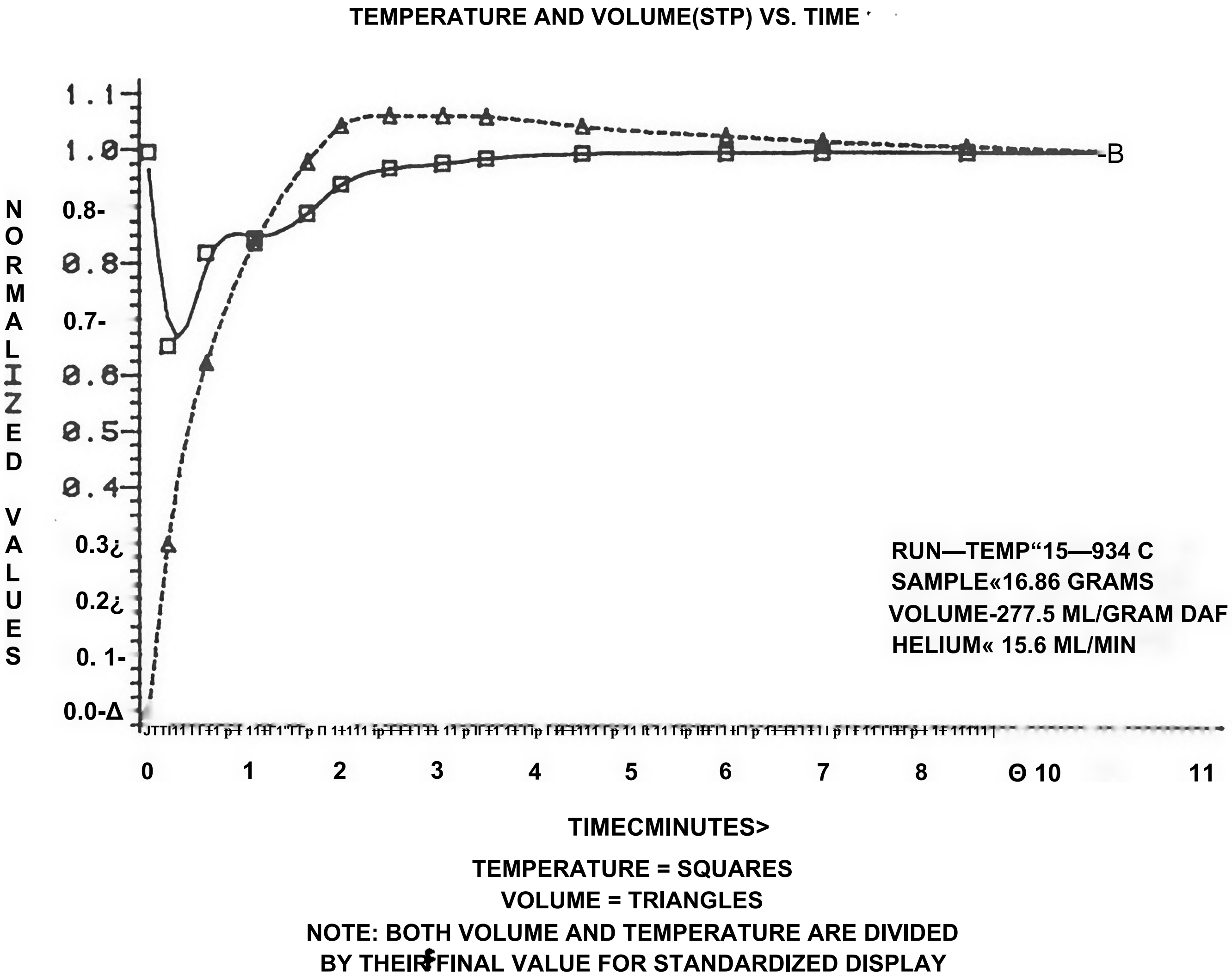
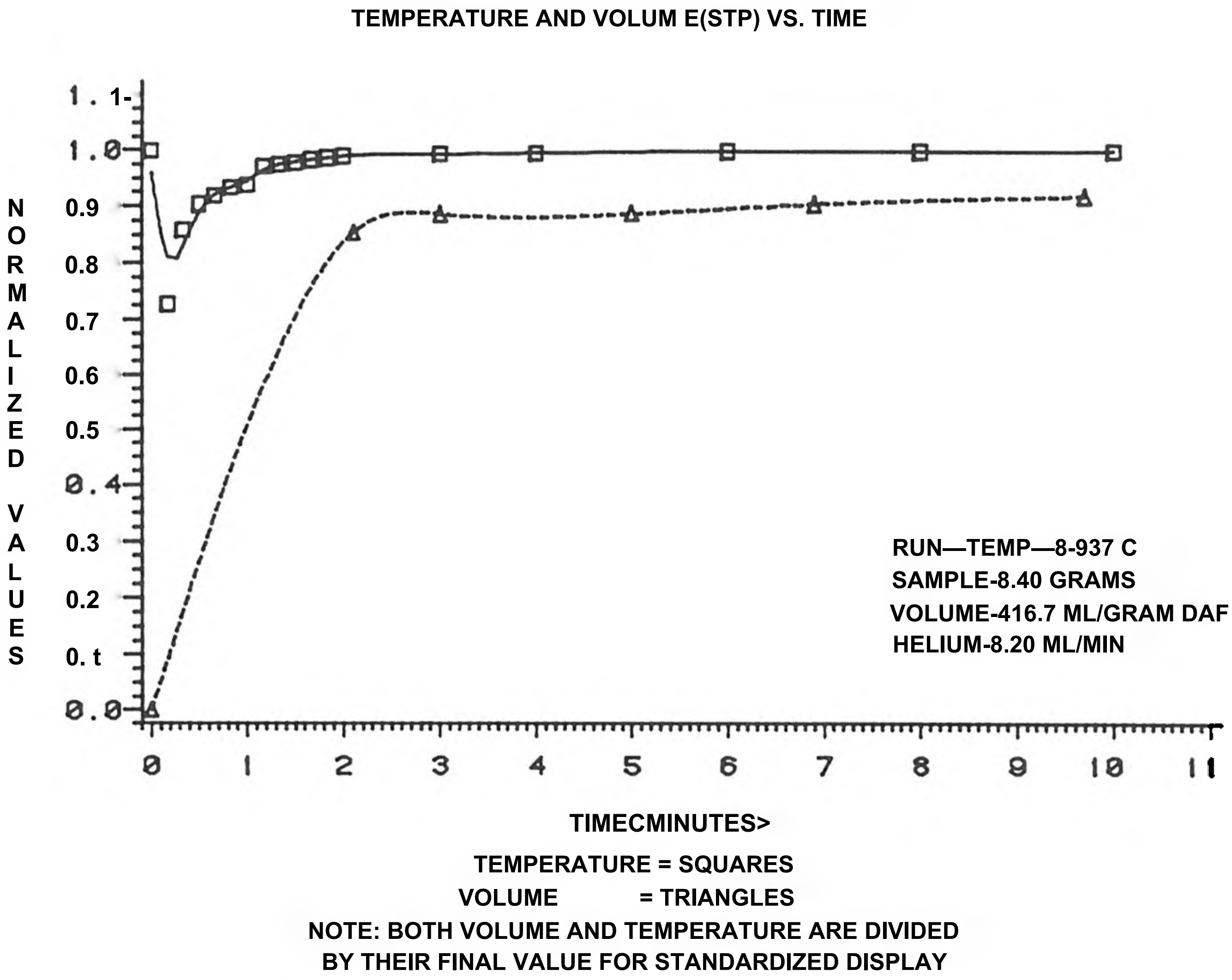

TEMPERATURE AND VOLUME(STP) VS. TIME
NORMALIZED VALUES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
TIME(MINUTES)
RUN-TEMP= 14-930 C
SAMPLE= 11.74 GRAMS
VOLUME=425.3 ML/GRAM DAT
HELIUM=8.40 ML/MIN
TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 37



TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 38



TEMPERATURE = SQUARES
VOLUME = TRIANGLES
NOTE: BOTH VOLUME AND TEMPERATURE ARE DIVIDED
BY THEIR FINAL VALUE FOR STANDARDIZED DISPLAY

Figure 39

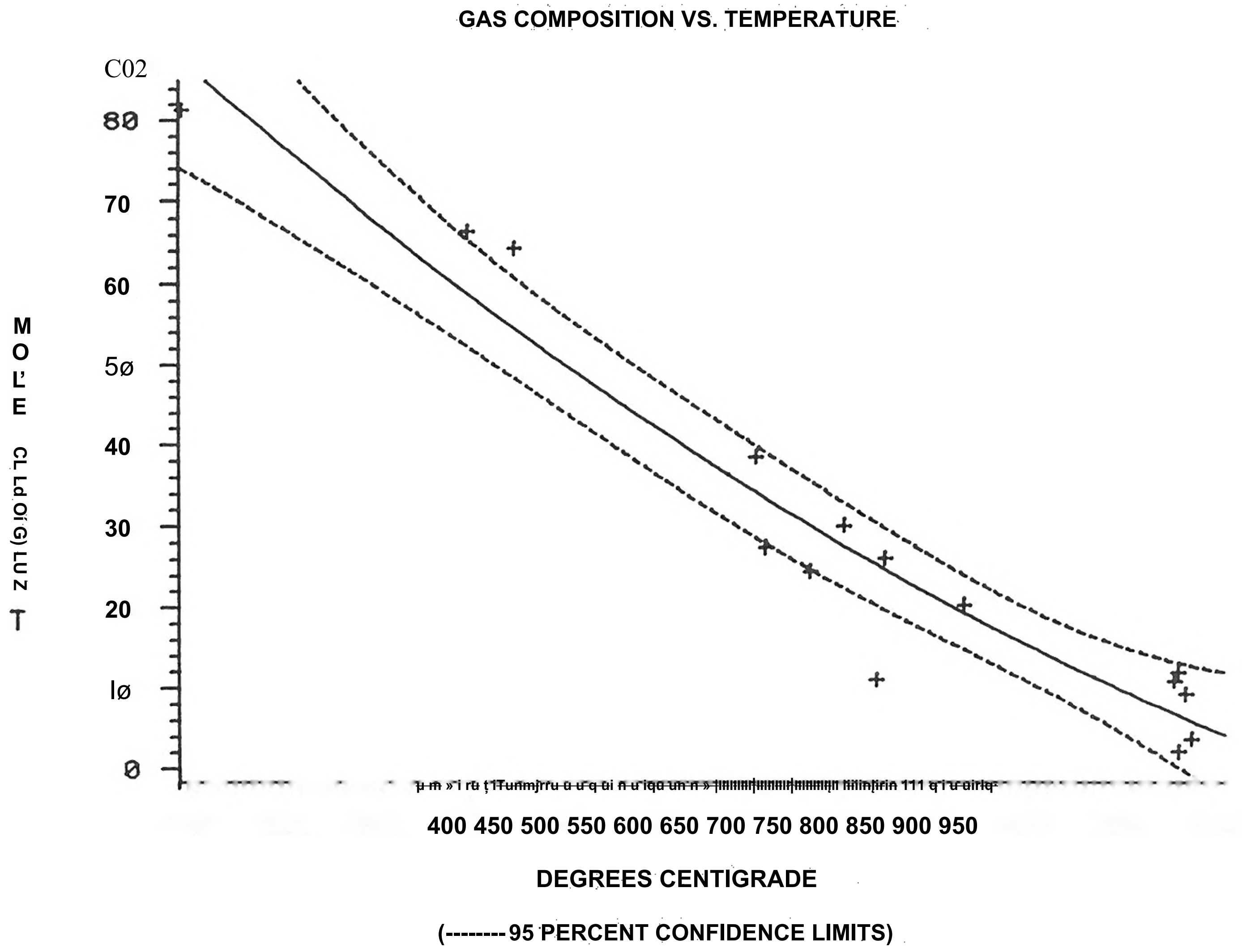

GAS COMPOSITION VS. TEMPERATURE
C02
80
70
60
50
40
30
20
10
0
MOLE PERCENT
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(--------95 PERCENT CONFIDENCE LIMITS)

Figure 40

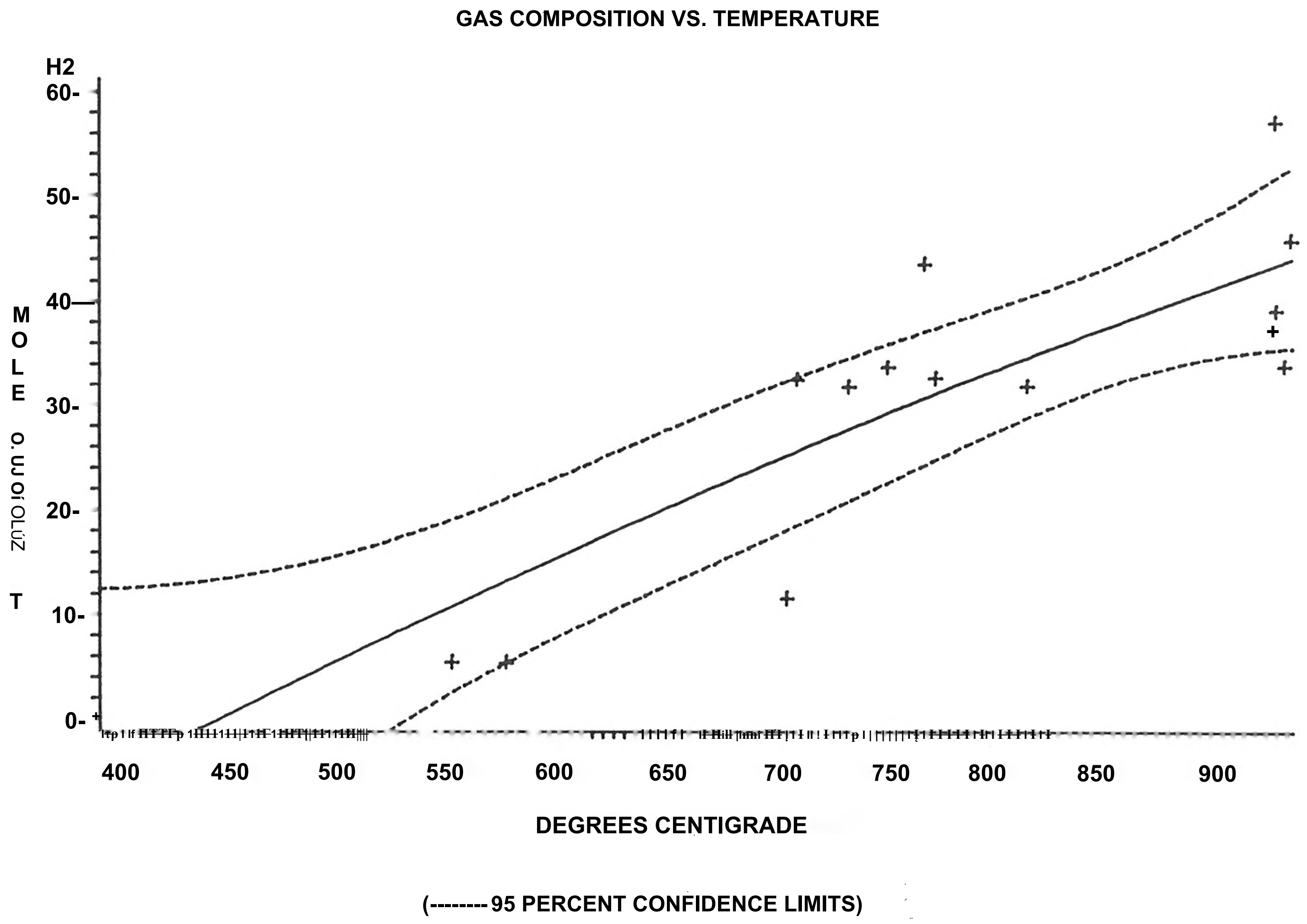

GAS COMPOSITION VS. TEMPERATURE
H2
60-
50-
40-
30-
20-
10-
0-
M
O
L
E
T
400
450
500
550
600
650
700
750
800
850
900
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 41

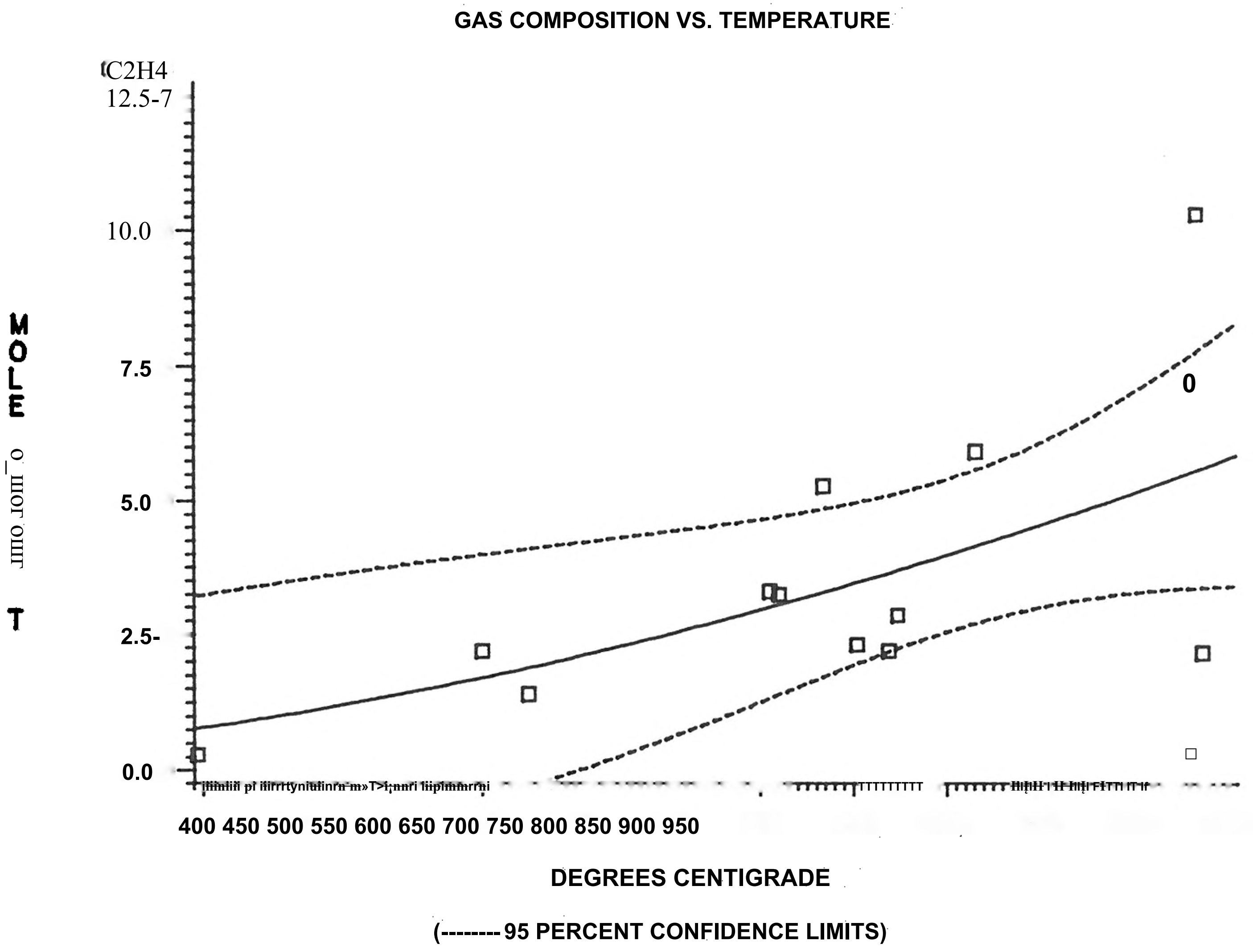

GAS COMPOSITION VS. TEMPERATURE
C2H4
12.5
10.0
7.5
5.0
2.5
0.0
MOLE
T
0
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 42

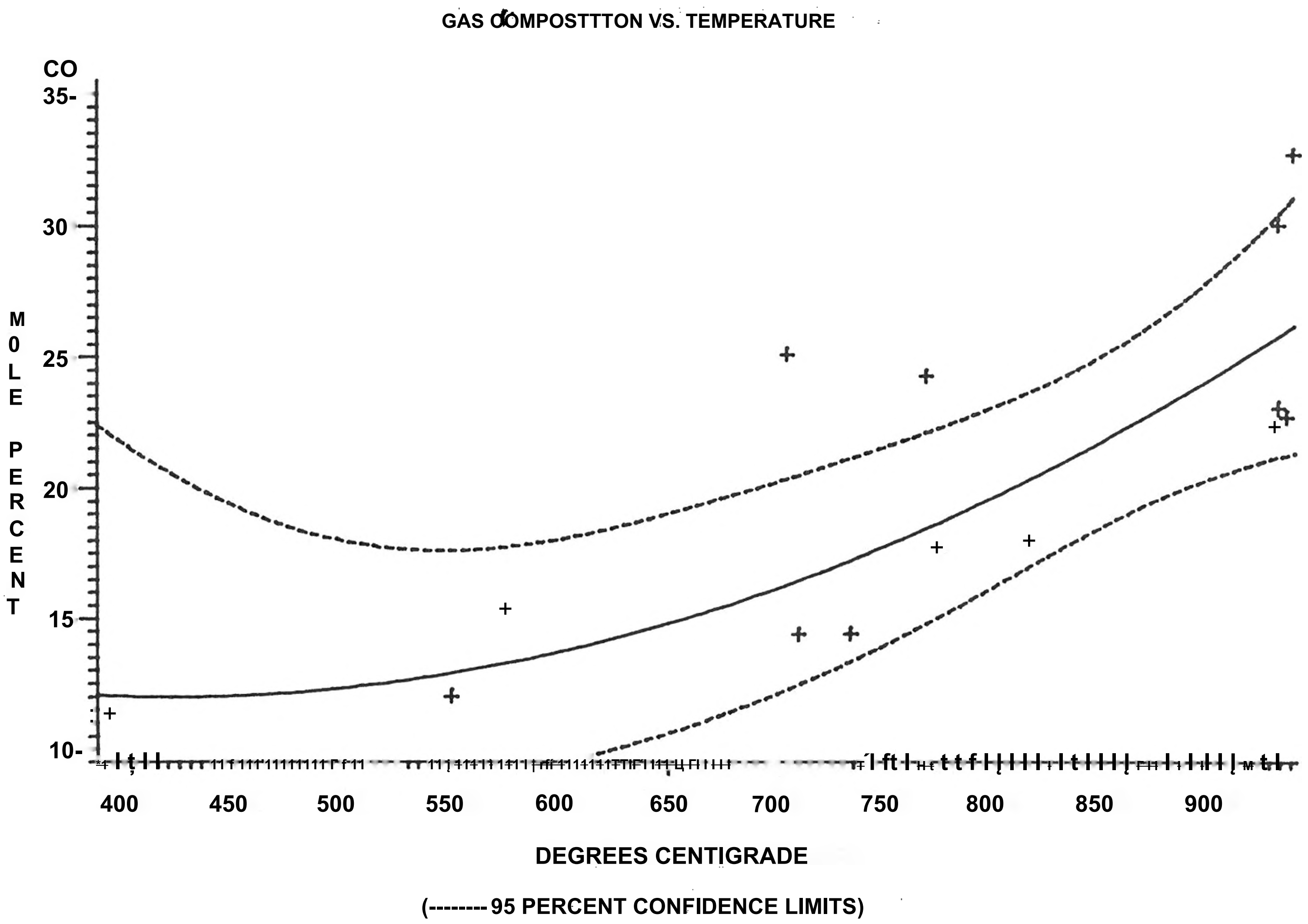

GAS COMPOSITION VS. TEMPERATURE
CO
35-
30
25
20
15
10-
MOLE PERCENT
400
450
500
550
600
650
700
750
800
850
900
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 43

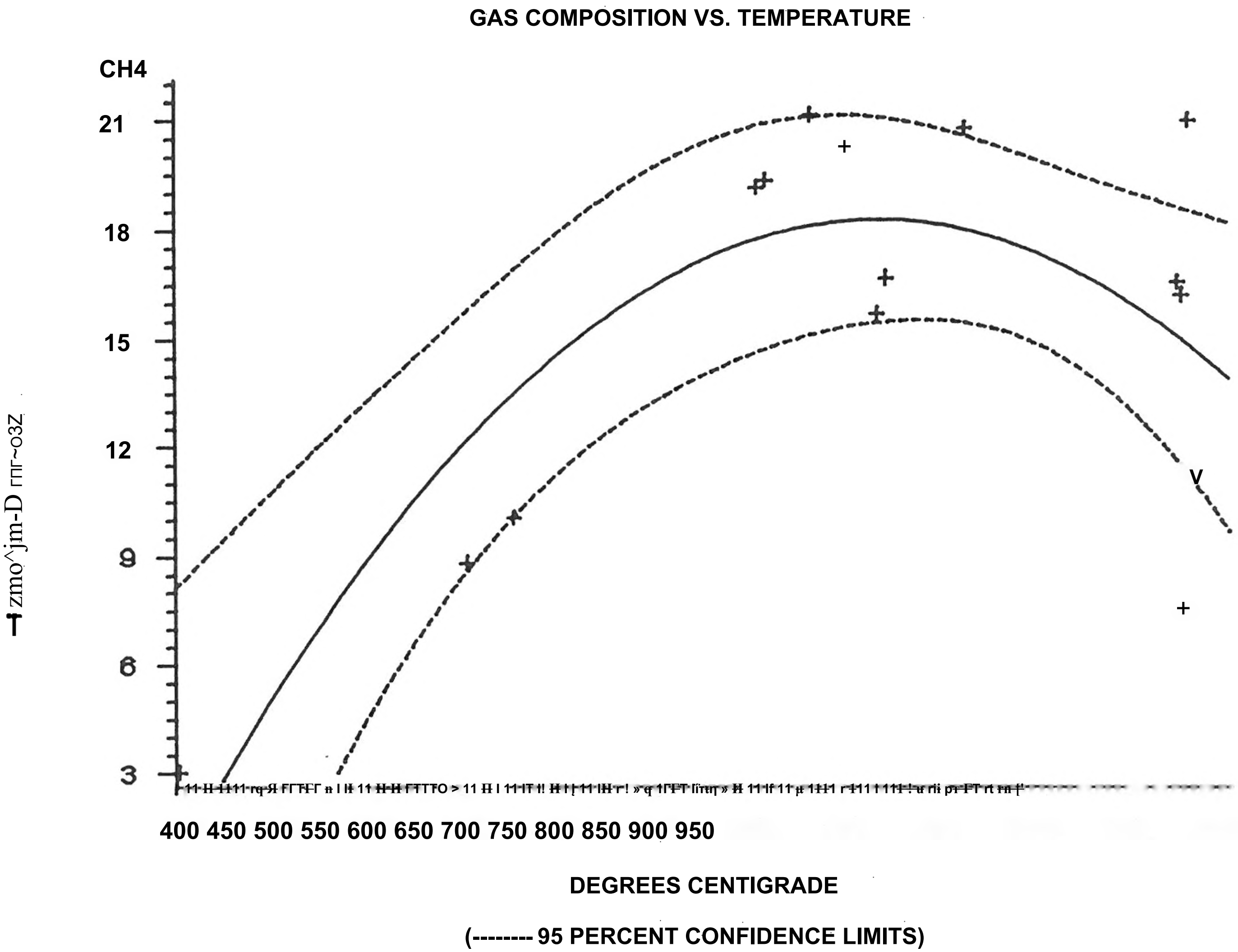

GAS COMPOSITION VS. TEMPERATURE
CH4
21
18
15
12
9
6
3
V
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 44

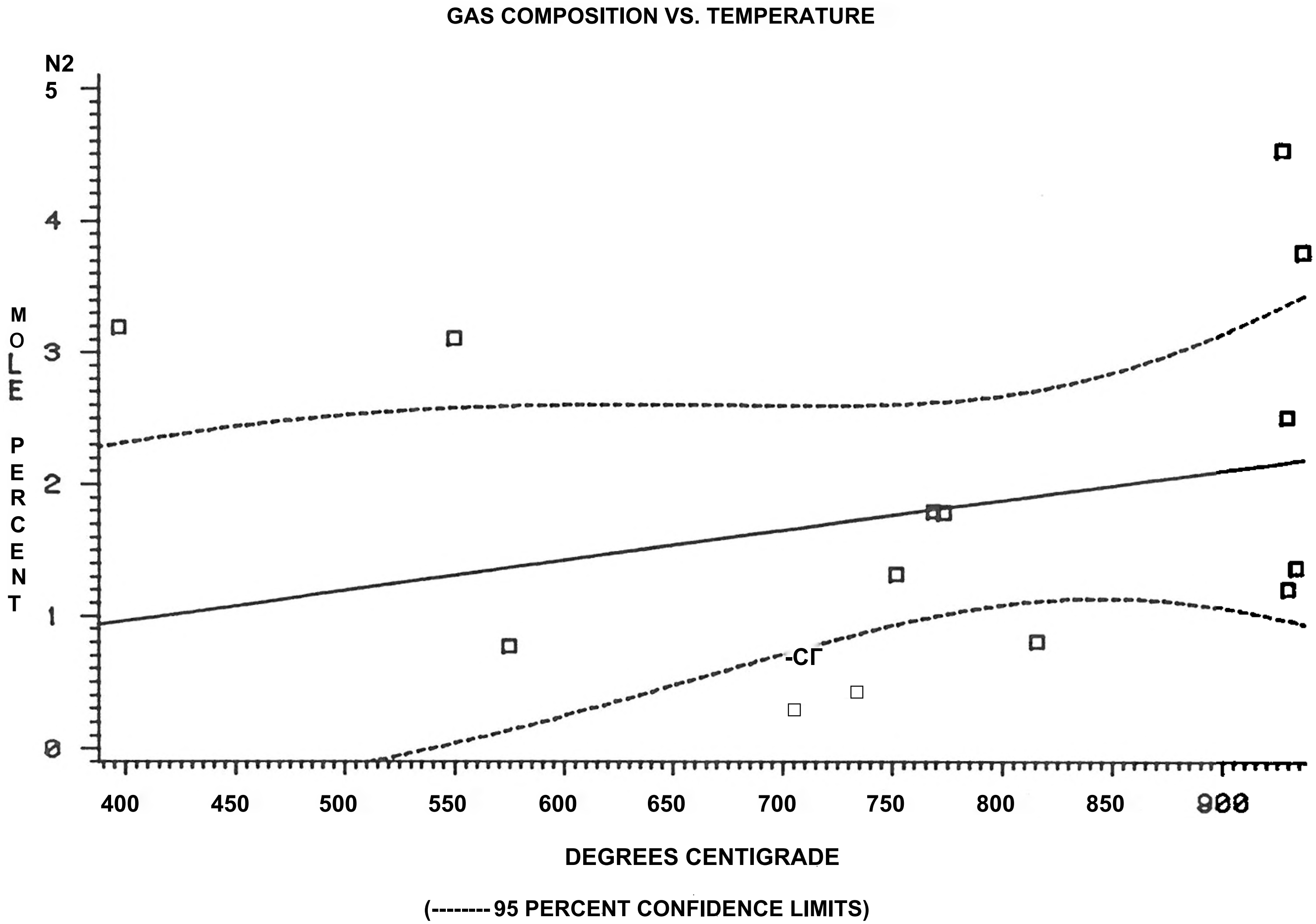

GAS COMPOSITION VS. TEMPERATURE
N2
5
4
3
2
1
0
MOLE PERCENT
400
450
500
550
600
650
700
750
800
850
900
DEGREES CENTIGRADE
(--------95 PERCENT CONFIDENCE LIMITS)

Figure 45

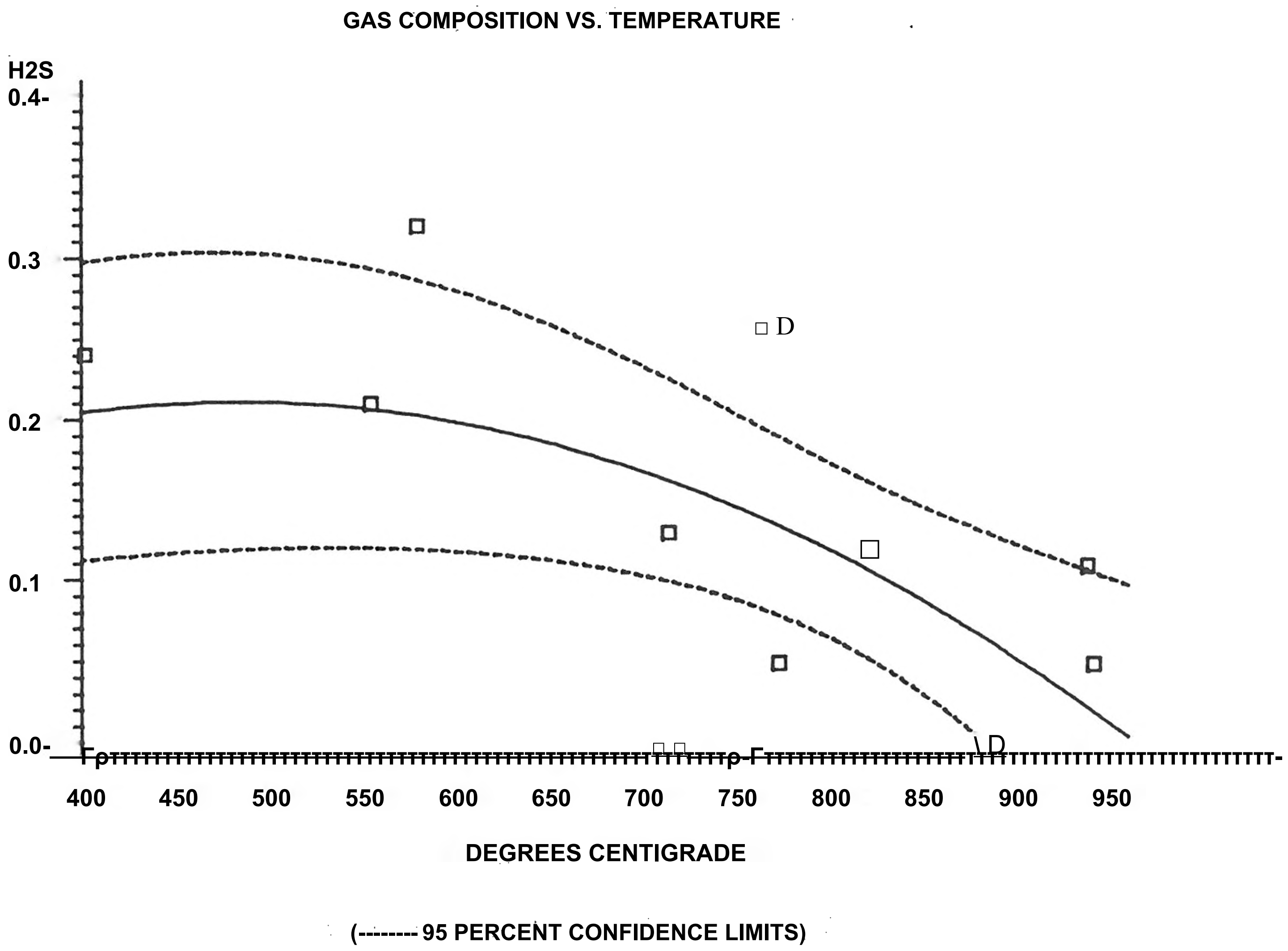

GAS COMPOSITION VS. TEMPERATURE
H2S
0.4
0.3
0.2
0.1
0.0
400
450
500
550
600
650
700
750
800
850
900
950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 46

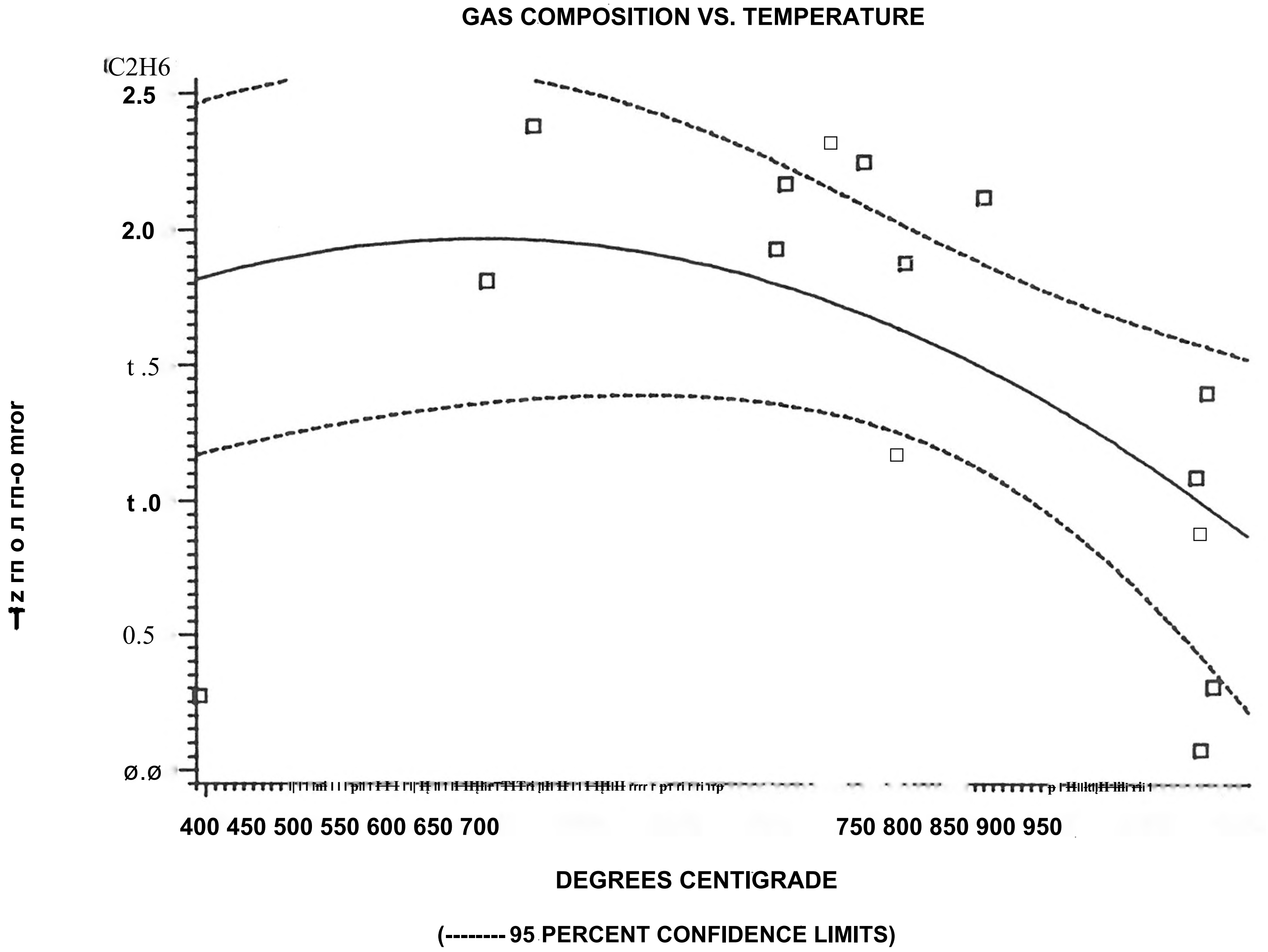

GAS COMPOSITION VS. TEMPERATURE
C2H6
2.5
2.0
1.5
1.0
0.5
0.0
400 450 500 550 600 650 700 750 800 850 900 950
DEGREES CENTIGRADE
(-------- 95 PERCENT CONFIDENCE LIMITS)

Figure 47