5-1984

The Low-Temperature Pyrolysis of a Nitrated North Dakota Lignite

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Spears,

Dennis Ross

1984

THE LOW-TEMPERATURE PYROLYSIS OF A NITRATED NORTH DAKOTA LIGNITE

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Dennis Ross Spears
May 1984

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THE LOW-TEMPERATURE PYROLYSIS OF A NITRATED NORTH DAKOTA LIGNITE

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ACKNOWLEDGEMENTS

To the following persons, I wish to express my humble gratitude and deepest appreciation:

The Standard Oil Company (Ohio) for sponsoring the cooperative education program under which this research was carried out, and for funding this project.

Charles Vandergriff, Jim Mortach, Phyllis Budinger, and especially Dr. Joe Kosman of the Standard Oil Company for their invaluable assistance in carrying out most of the analyses contained in this study.

Dr. George F. Salem, Jean Jeffers and Michael Epstein of the Pyrolysis Group of The Standard Oil Company for their greatly appreciated assistance in completing this project.

Dr. Alan A. Leff of the Standard Oil Company for suggesting and overseeing this research and for making completion of this study much easier.

Carol Reagles of the Mathematics Department of Western Kentucky University for her help in setting up the statistical analyses.

Robert Cobb and Dr. Jay Sloan of the Academic Computing and Research Service of Western Kentucky University for their "bend-over-backwards" attitude in doing the regression analyses and graphings for this paper.

Dr. William G. Lloyd and Dr. Rita K. Hessley for serving on my thesis committee and for their guidance in the preparation of this paper.

Dr. Laurence J. Boucher for two years of patience, encouragement and first-class guidance.

Judy Campbell for typing the final manuscript and keeping the fun in chemistry.

Dudley, Margaret, and Rene' Spears for their encouragement and help in getting me this far.

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Dennis Ross Spears 81 pages

Directed by: Alan A. Leff, The Standard Oil Company, Cleveland, Ohio; L. J. Boucher, W. G. Lloyd, and R. K. Hessley

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Low-temperature pyrolysis is the thermal degradation of coal in an inert atmosphere at temperatures below 700°C. Coal pyrolysis is well-studied, being a complex mix of many reactions. Pyrolysis is affected by changes in many different process variables, such as temperature, pressure and heating rate. Low-temperature pyrolysis is an old and well-studied process.

Chemical pretreatments have been used to beneficiate conversion processes, inducing pyrolysis. Nitration has not been one of them. Pyrolyzing a nitrated coal would, hopefully, rapidly devolatilize the coal and break up the matrix into more commercially usable products. The nitration procedure developed by The Standard Oil Company minimizes oxidation of the coal, reducing the adverse affects of such a treatment.

Lignite, both untreated and nitrated at two different levels, was pyrolyzed at temperatures of 250, 425 and 600°C, helium pressures of 0, 500, and 1000 psig, with sample masses of about 1, 3, and 5 grams. Residence times of 0.5, 1.5 and 2.5 hours were used. The yields of volatiles (gas), oils, asphaltenes, preasphaltenes, and char were monitored. The char was subjected to elemental analysis, and the pyrolysis gas was analyzed by gas chromatography.

Nitration does not appear to improve lignite low-temperature pyrolysis substantially. Nitrated and untreated lignites produce similar char and oil yields. After nitration the char nitrogen content is raised substantially, and the hydrogen content of the char is decreased. Nitration does not cause the expected rapid devolatilization, nor does it substantially improve the quality of the off-gas. Nitration does de-ash and desulfurize the coal.

CHAPTER I

INTRODUCTION

Coal pyrolysis is not a new technique. It has been used for almost two hundred years to obtain saleable products from coal, such as coke, chemical feedstocks and combustible gases. With the advent of petroleum and natural gas in the early part of this century, industrial interest in coal pyrolysis as a means of supplying chemical feedstocks or synthetic fuels waned.

The Arab oil embargo of the early seventies renewed industry's interest in pyrolysis. Since that time, several industrial-scale pyrolysis processes have been developed, such as the TOSCO and COED processes.(1) However, these processes are presently not economically feasible.

In 1982, Dr. G. F. Salem, Dr. A. A. Leff and Bob Sherrard of The Standard Oil Company (Ohio) developed a means of nitrating coal with minimal oxidation.(2) The idea was to turn coal into a "TNT-like" material which would explode or rapidly devolatilize under pyrolysis conditions, hopefully breaking up the coal matrix into commercially usable fragments while lowering the char yield.

In order to determine the behavior of a nitrated coal as opposed to an untreated coal under pyrolysis conditions, this study was initiated. Low-temperature carbonization conditions were used because of the equipment on hand and because preliminary studies by Sohio researchers indicated that high-temperature conditions were unnecessary.(3) A well-characterized North Dakota lignite was chosen because it was on hand, because the nitration process should oxidize lignites less than higher rank coals, and because its structure was amenable to producing substituted mono-aromatics when pyrolyzed.

As a part of this study, the effects of varying the sample mass, initial pressure in the reactor, the temperature and time of pyrolysis were examined in order to have a basis of comparison with other pyrolysis studies. The effects of these parameters and the level of nitration of the base coal on the yield of gas, oils, asphaltenes, and residual char, as well as the ultimate analysis of the char and contents of the off-gas, were determined.

CHAPTER II

HISTORICAL

Pyrolysis is defined as the thermal decomposition of a substance in an oxygen-free atmosphere.(4) Coal pyrolysis is often referred to as carbonization or destructive distillation; the latter is used especially in older literature. Pyrolysis of coal is considered to be low-temperature when carried out below 700°C, and is considered to be high-temperature when executed above 900°C. Intermediate temperature carbonization is the pyrolysis of coal between 700 and 900°C. These temperatures are not exact delineators, but only rough guidelines.

Low-temperature coal pyrolysis is not a new process. In 1792, a Scottish engineer named Murcoch distilled coal in an iron retort to produce gas to light his home. By the early 1800's, gas distilled from coal was used for illuminating city streets all over the world. The first major city to be so lit was London, in 1812.(5)

Coal gas, or "town gas," was produced from retorts which yielded coke as a secondary product. This coke was suitable for varied industrial, residential and commerical uses, yet not for use in iron smelting.(6) However, carbonization processes for producing metallurigical coke were common by the mid-nineteenth century.

Along with the discovery of the utility of gases from coal distillation came the discovery of the utility of tar produced from dry coal distillation. Until petroleum came into use, coal tar served as one of the world's primary sources for organic chemicals. Joseph Lister discovered phenol's disinfectant properties in 1868; the source of his phenol was coal tar.(7) Through his use of coal tar extracts, Sir William Perkin helped develop the aniline-dye industry.(8) Later, sulfua drugs were developed from compounds found in coal tar.(9)

Because coal pyrolysis was being used so much, in so many ways,with so many coals,standard assays were developed. Three major assays for low-temperature carbonization have come into prominence: the Gray-King assay, the Fischer assay, and the Bureau of Mines Oil-Shale assay. These assays are thoroughly reviewed and compared by Davis and Galloway.(10)

In the Gray-King assay, 20 grams of -60 mesh coal are heated to 300°C inside a horizontal glass tube, the temperature is allowed to stabilize, then the coal is heated to 550°C and held there for one hour. In the Fischer assay, 250 grams of -10 mesh coal are heated to 550°C at a rate of about 9°C/minute. The coal is held at 550°C until gas evolution ceases. The Bureau of Mines assay is similar to the Fischer assay; a charge of 225 grams of -10 mesh coal is placed in an iron retort similar to Fischer's apparatus. The coal is heated until the distillate ceases to be evolved. Of the three, the Fischer method appears preferable on the basis of its accuracy and ease of manipulation.(10)

Literally countless assays of coals of every rank have been done by scientists all over the globe. To discuss even a fraction of them would require a lengthy discussion; however, a few of these assay studies are mentioned below, along with a general summation of the results of these assays on lignite.

When studying the three standard pyrolysis assays, Davis and Galloway assayed thirteen western United States lignites. Using the Fischer assay, they obtained the following results: 41.8 to 58.4% coke, 2.5 to 5.8% tar, 5.8 to 11.8% gas. The gas yields consisted of 19.0 to 55.3% CO_2, 15.4 to 37.9% CH_4, 9.7 to 17.3% H_2, 7.0 to 13.4% CO, and smaller amounts of ethene, ethane, and molecular nitrogen and oxygen.(10)

Muller, Graf, Gruber and Scheuch did Fischer assays on a variety of Austrian coals, including twelve lignites. These lignites yielded 49.3 to 58.0 wt-% coke, 7.3 to 20.1 wt-% tar, and 17.0 to 23.8 wt-% gas. Higher-ranked coals gave more coke and tar, but less gas.(11) Undoubtedly, these results stem from the higher volatiles content of lower-ranked coals, as well as the greater degree of coalification of the higher-ranked coals.

In December of 1953, the U.S. Bureau of Mines released the results of a series of distillation assays on Missouri River Basin coals. Using a procedure they and other USBM researchers developed (which is similar to the Oil-Shale assay), they pyrolyzed their samples at 500°C. On a dry, ash-free basis, the twelve lignite samples yielded from

66.3 to 73.5% char, 5.1 to 9.4% tar plus light oils, and 10.3 to 15.8% gas. The sub-bituminous and high-volatile C bituminous coals that Gomez and Goodman assayed yielded, as is typical, more char and tar plus light oils, and less gas. They found that sub-bituminous coals assay much like lignites; they also found that for all coals studied, the light oil yield was essentially constant, an average yield being about 1.5%.(12)

Two assays of South Arcot lignite have been run. The assay by Subrahmanyan and Nair carried out at 500°C on a 29 gram charge of coal yielded 58.6% char, 10.2% tar, and about 21% gas (16 liters). Of interest is the detection of trace amounts of ammonia generated during the assay.(13) While ammonia production from coal is not unusual,(14,15) ammonia is not a gas commonly thought of in conjunction with coal carbonization.

The other assay on South Arcot lignite was executed by Ratnam and Veeraraghavan. They made briquettes of -60 mesh South Arcot lignite, but did not use a binder. At a carbonization temperature of 500°C, on a dry, ash-free basis, these researchers obtained a char yield of 53.9% and a tar yield of 10.2%. These results are comparable to other lignite assays.(16)

Sustmann and Lehnert pyrolyzed a lignite from Geiseltal and then de-ashed a sample of the same coal with 0.9 N HCl. They pyrolyzed the de-ashed coal sample also. The untreated lignite contained 9.87% ash, and the de-ashed coal contained

0.88% ash. The low-ash coal yielded more char, water and slightly more tar, but substantially less gas than the untreated lignite. The off-gas of the low-ash coal pyrolysis yielded less CO_2 and H_2, much more CO and about the same percentage of O_2, N_2 and hydrocarbons.(17)

One other study is worth mentioning because in procedure it differs radically from the investigations just discussed. Since the late 1950's, low-temperature, low heating rate carbonization studies have become fewer and fewer. High-tmperature and/or high heating rate studies have come into vogue. One such study by Cliff et al. is typical. They pyrolyzed a sample of -45 μm samples of Yallourn brown in a shock-tube pyrolyzer and -106 + 90 μm samples of the same coal in a fluidized-bed pyrolyzer. Yields of 58% char and 18% tar (both on a dry, ash-free basis) were obtained from the fluidized-bed pyrolyzer. At 500°C, the fluidized bed pyrolyzer yielded 3% CO and 7% CO_2; the shock0tube pyrolyzer yielded no CO or CO_2 at this temperature. The fluidized-bed pyrolyzer had a residence time of about 0.5 seconds and the shock-tube pyrolyzer had a one millisecond reaction time.(18) Note the higher tar yields in this study than in the previously discussed assays.

A great deal of effort has been put into examining the effects of different process variables, such as heating rates and pyrolysis temperature, on coal pyrolysis. The purpose of these studies has been to discover both the importance of various paramters and to find their optimal value for peak char, tar and gas yields, for best quality of the char, tar and gas. Of all the parameters studied so far, temperature seems to play the key role.(19)

The temperature of pyrolysis, sometimes referred to as the "soak temperature," affects the tar yield, both in quality and quantity. Tar yields, in general, show a gentle maximum at about 560°C; at higher temperatures, the tar degrades to form char and gas.(19) Low-temperature tars have few components in amounts greater than 0.5%, whereas high-temperature tars (from carbonizations at greater than 700°C) are more homogeneous and more aromatic in nature, containing predominantly benzene, toluene and xylene.(1) Char yields appear to decrease with increasing pyrolysis temperatures.(16)

Temperature affects the elemental composition of the char. When Reynolds et al. pyrolyzed a lignite from Ward County, North Dakota, they found that in the 500 to 800°C range, (on a dry, ash-free basis) carbon content of the char slowly increased with temperature. The hydrogen, nitrogen and oxygen content in the char dropped rapidly with higher pyrolysis temperatures. These results were similar to those found from the pyrolysis of a Wyoming low-rank coal.(20) Rammler, von Alberti and Fischer assayed a Böhlen lignite and a Kleinleip coking coal and found similar results to those of Reynolds' group.(21)

Temperature affects the composition of the off-gas of coal carbonizations. Reynolds et al. found that as the soak temperature was raised from 500 to 1000°C, H_2 and CO yields increase, and the yields of CO_2, methane, ethane and

H_2S are lowered. The yield of illuminants, or unsaturated hydrocarbons, shows a gentle maximum in the 800 to 900°C range.(20) When a Wyoming sub-bituminous coal was assayed at temperatures ranging from 300 to 1000°C, the analysis of the off-gas was found to follow the trends shown in Figure 1.(5)

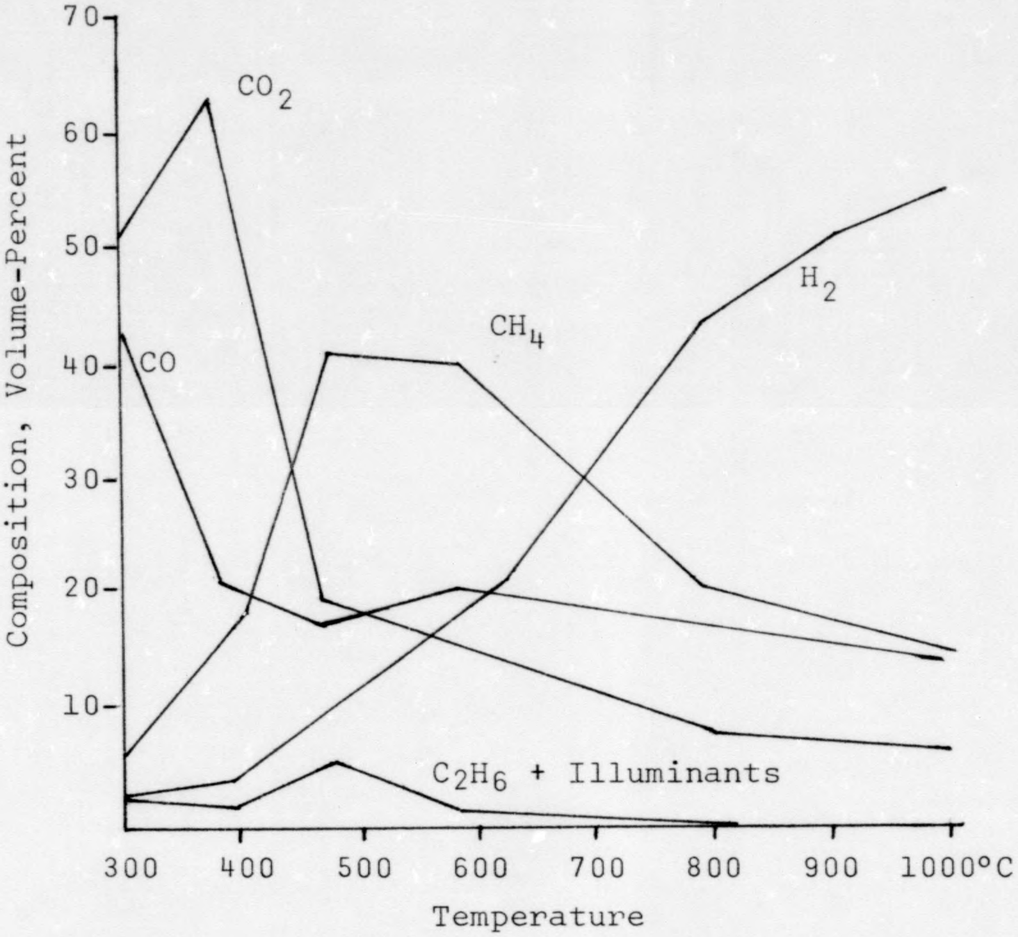


Figure 1. Composition of pyrolysis gas of Wyoming sub-bituminous coal assayed as different temperatures.

Heating rates are also important in pyrolysis. The time a pyrolysis reaction takes to reach a given reaction temperature plays a key role in the yields of char, liquid products, and gaseous products. Wen and Dutta have classified heating rates as shown in Table 1. Table 2, also compiled by Wen and Dutta, shows suggested temperature programming modes for maximizing the yield of a desired product.(22)

TABLE 1

Classification of Heating Rates for Pyrolysis

Type	Heating Rate, °C/s
Slow Heating	1
Intermediate	5 to 100
Rapid Heating	50 to 100, 000
Flash Heating	10^6

TABLE 2

Suggested Temperature Programming Modes for Maximizing Yields of Desired Products.

Desired Product	Heat Rate	T°C of Pyr.	Solid Res. Time	Volatiles Res. Time
Tar	Rapid	500	Long	Short
Liquid	Rapid	750	Long	Long
Gas	Rapid	1000	Long	--[a]
Methane	Rapid	600	Long	--
Hydrogen	Rapid	1000-1100	Long	--
Illuminants	Flash	1200	Long	Intermediate
CO	--	750	Long	--

a = effect either unknown or insignificant

The effect of temperature has already been discussed. Notice that Table 2 contains no mention of slow heating. Show heating rates allow the tar to polymerize and form char. This same effect is noticed when the residence time of the volatiles and tar is increased, since these components are exposed for longer periods of time to the severe environment of the reactor. High heating rates necessarily decrease the char yield.(19) These facts have caused a great emphasis to be placed on rapid- and flash-pyrolysis techniques in the last decade.

The effect of residence time is related to the effects of soak temperature and heating rate. Table 2 shows that long residence times, or "soak times," for the coal solid are always recommended to obtain maximum yields of volatile materials and tar. The primary degasification phase of pyrolysis is generally rapid and thus yields of material produced during this stage of pyrolysis are not heavily dependent on solid residence times. However, the active thermal decomposition and secondary degasification phases are shower; therefore, increased solid residence times result in decreased char and increased gas yields.(19) Ideally, then, to produce tar or gaseous products, long heating of the solid (to thermally decompose it) and short residence times for the volatiles (to keep them from polymerizing) would produce the greatest amount of volatile material.

The effect of pressure on coal pyrolysis has been examined. Sustman and Ziesecke have reviewed work in this area prior to 1939.(23) In 1940, these men published a study on the pressure pyrolysis of four German coals at low-temperature carbonization conditions; one of these coals was a lignite from Saxony. At 600°C, this lignite showed the definite trends from 1 to 50 atmospheres of pressure. At higher perssures, char yield, total gas yield, and the methane yield are increased, while the yields of tar, light oils, H_2, CO, CO_2 and N_2 are lowered. Molecular oxygen yields appear to be independent of pressure.(24)

Increasing the pyrolysis pressure appears to hold the volatilized organic molecules in the reactor, thus cracking them and accounting for higher has yields.(25) By the same token, since these volatile organics are held in the reactor (and undoubtedly inside the coal solid), where they would have an opportunity to polymerize, the char yields would increase with pressure.

Pressure increase effects on gas composition are also similarly explained. The increase in yield of methane and higher analogs (ethane, propane, and so forth) at elevated pressures is a sure sign of cracking. So is the decrease in H_2 yield. The decrease in CO_2, CO and N_2 yields at elevated pressure appear to be due to the operation of Le Chatelier's principle.

The effects of sample mass on coal pyrolysis have not been well studied, but it is known that increasing the amount of coal present causes it not to heat as well, due to the low thermal conductivity of coal. This fact is the basis behind the development of fluidized-bed pyrolyzers and combustion furnaces. Larger sample masses, if used in the same reactor, inhibit devolatilization, apparently for the same reason.(26)

The particle size of the pyrolyzed coal may affect the outcome of the carbonization reaction. Large particles have a thermal gradient when heated, that is, they heat faster on the outside of the particle than on the inside. Small particles are heated essentially uniformly. Size does not appear to affect yields below a particle size of about 50 micrometers.(5)

The rank of a coal plays an important role in its carbonization behavior. Low-rank coals yield more gaseous material and less char, since the matrix of such coals is less condensed and has a high content of easily-volitized ring substituents. Lignites and high-volatile C bituminous coals give the greatest yield (under Fischer assay conditions) of tar and light oils. The tars of lignites are less aromatic than those of bituminous coals.(1) Graphic representations of the way rank affects pyrolysis yields and the composition of the off-gas are shown in Figure 2 and Figure 3, respectively.

While coal pyrolysis has been tried in conjunction with different chemical pretreatments, nitrated coal has not reviously been pyrolyzed prior to the research of Salem, Leff and Sherrard.(2) Coal has been treated with nitric acid, but never before has nitration been used as a means of enhancing pyrolysis.

Treatment of bituminous coals with $LiAlH_4$ increases their swelling index. Pyrolytic decompositions of coal which has been either naturally or artificially oxidized show

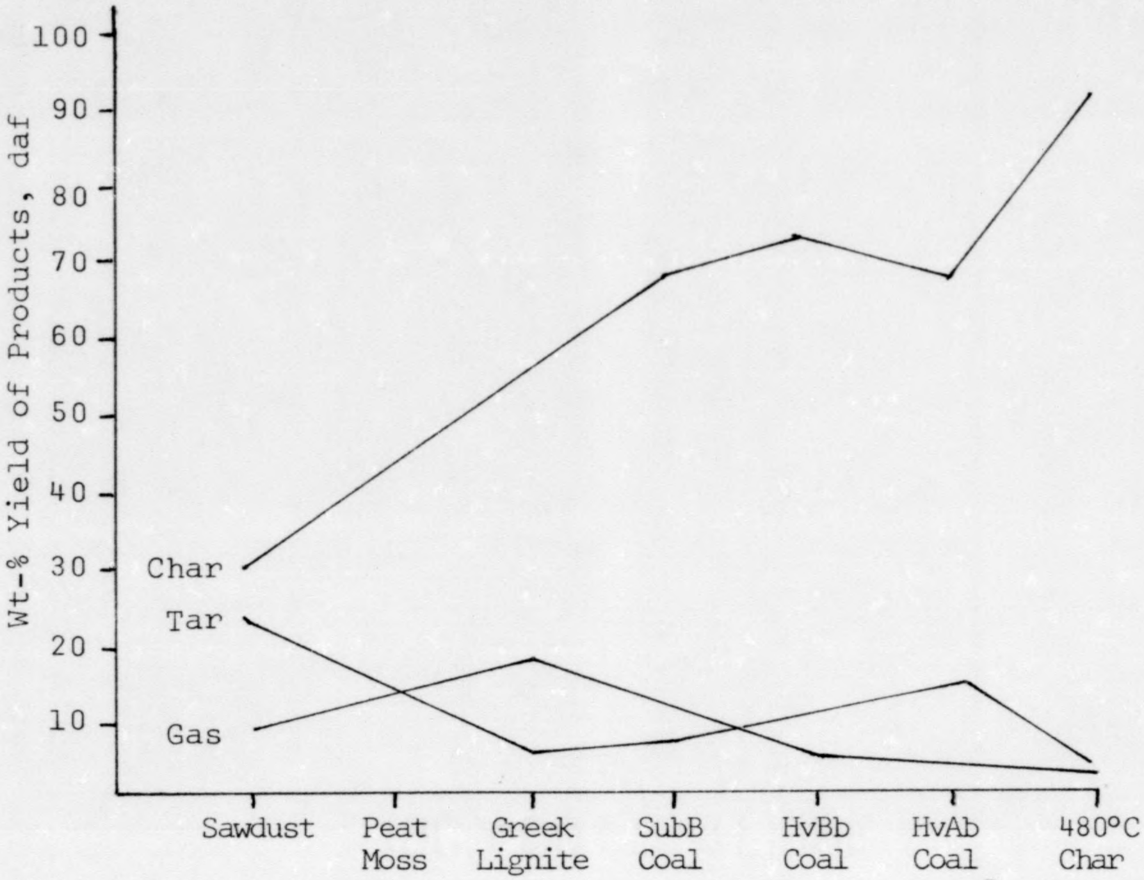


Figure 2. Product distribution dependence on rank.[5]

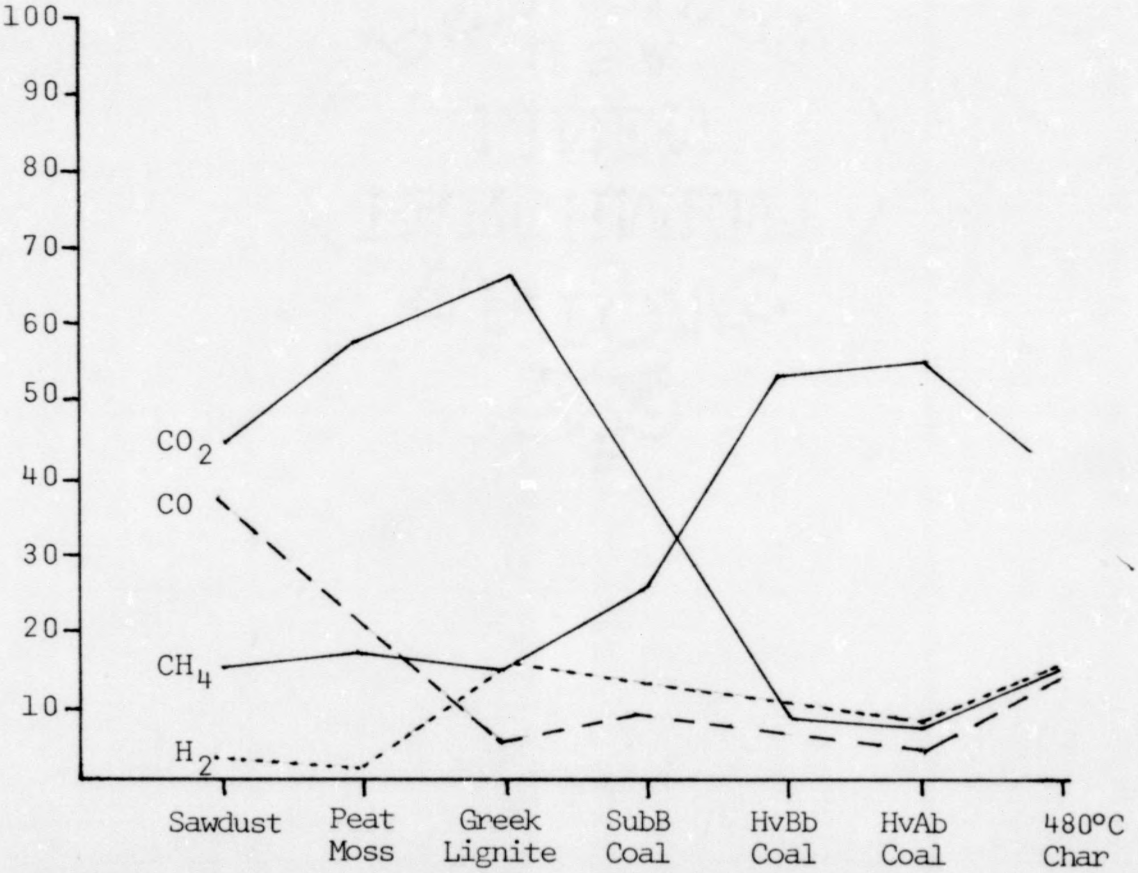


Figure 3. Pyrolysis Gas Composition Dependence on Rank (O_2, N_2-free basis).[5]

general agreement on the effects exhibited, which include increased yields of carbon oxides and water, decrease in tar yields and changes in the coal's plastic properties.(4) Thus, a process in which oxidation is minimized is important to successful coal pyrolysis.

The kinetics of pyrolysis is very involved and many-faceted. Yet pyrolytic decomposition has been modeled, surprisingly, by a simple pseudo first-order equation (Equation 1).

$$\frac{dV}{dt} = k(V - V) \qquad (1)$$

Here, the rate of volatiles production is proportional to the remaining volatile fraction of the undecomposed coal. However, differences in rank, soak temperature and heating rate can generate radically different values.(5) Numerous modeling equations have been generated to describe all facets of pyrolysis and its reactions, but they are not necessarily applicable to all situations.(22)

As has already been stated, in its purest sense coal pyrolysis is a thermal process executed upon coal with no reactive species present other than the coal itself. Lignite, because of its large volatiles content, its numerous and varied ring substituents, and its loosely connected, less condensed matrix, is very susceptible to thermal degradation. In such a heterogeneous material as lignite, many reactions take place; to catalogue them all would be a feat indeed.

Nevertheless, some of the more common thermal reactions can be described.

Coal pyrolysis takes place in four phases. Phase one is the primary degasification phase, in which chemisorbed gases and water and other small molecules are removed from the coal. This phase takes place in the temperature range of below 350°C. From 350°C to about 550°C, coal enters the second phase of pyrolysis, active thermal decomposition. The matrix begins to break up during this temperature period, with the more easily thermolyzed cross-linkages being severed. During this phase, tar and water from organic decompositions are generated. The final phase of coal decomposition, the secondary degasification phase, occurs between temperatures of about 550 and about 1400°C. During this phase, the decomposed coal begins to break up into low molecular-weight molecules, such as carbon oxides, molecular hydrogen, and short-chain hydrocarbons.(27) The fourth phase, which occurs at temperatures above 1400°C, is that of ring fusion. During this phase, radical species combine with one another to form char, as hydrogen-containing species are no longer readily available.

During pyrolysis, it is probable that many parallel and series reactions take place. This is especially true of the active thermal decomposition phase. This phase is a free-radical process to a large degree. Coal itself contains free radicals which apparently have existed for millions of years; the radicals are stabilized by the aromaticity of coal and its existence in the solid state. Coal contains many bonds which, if thermolyzed, would tend to form free radicals. Figure 4 is a generalized mechanism for the reaction of free radicals.

CHAIN INITIATION:

$$R\text{--}R' \longrightarrow R\cdot + R'\cdot \qquad (2)$$

CHAIN PROPAGATION:

$$R\cdot + R''H \longrightarrow RH + R''\cdot \qquad (3)$$

CHAIN TERMINATION:

$$R\cdot + R''\cdot \longrightarrow R\text{--}R'' \qquad (4)$$

Figure 4. A General Mechanism for Free Radical Reactions.

As long as readily extractable hydrogen atoms are present, tar, light oils, and gaseous hydrocarbons will be evolved. When such atoms no longer become available, then the radical species liberated by pyrolysis will combine and cause the formation of char.

Fuchs and Sandhoff presented a model of the pyrolysis of a bituminous coal. The model, reproduced in Figure 5,is a visual example of some of the many reactions which take place in coal pyrolysis.(4) Lignite pyrolysis differs from this model chiefly in that lignite is much less condensed than bituminous coal, and it has many more ring substituents, especially phenolic and carboxylic groups.

Nitrated lignite differs in its pyrolysis due to the presence of numerous R-NO_2 species. Under normal circumstances, nitrogen is present in coal in amounts of about 1% and is found chiefly in the form of cyclic amines. The nitro group is essentially nonexistent in coal.

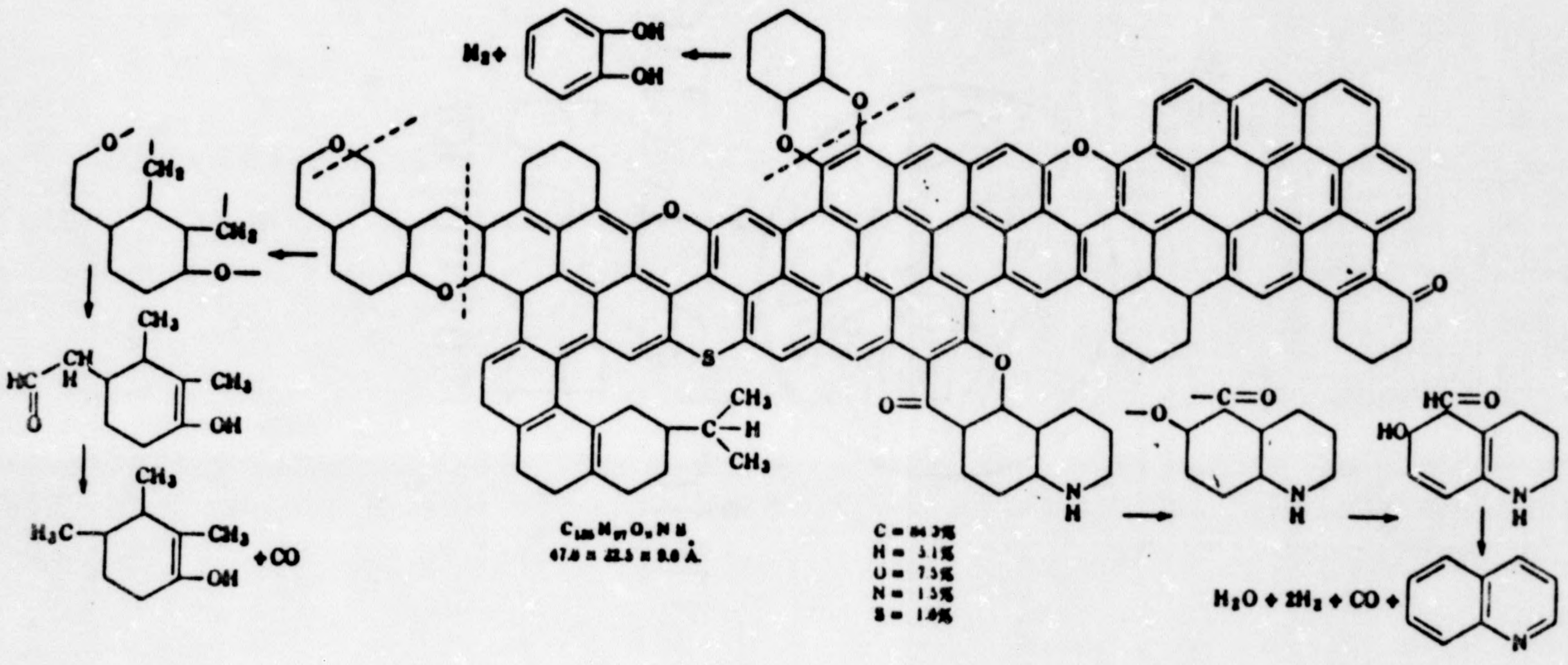


Figure 5. Fuchs and Sandhoff Model of Pyrolysis.

The thermal reactions of nitro compounds have been of interest since trinitrotoluene was first used as an explosive in 1890.(28) Nitrating lignite before pyrolysis should synthesize a substance which would behave like 2,4,6-trinitrotoluene and would "blow up" during pyrolysis, thus breaking up the matrix into commercially usable fragments.

Trinitrotoluene, the best known nitroaromatic compound, explodes at 240°C.(29) When pyrolyzed, nitroaromatics appear to form free radicals. For example, if nitrobenzene is pyrolyzed for twenty seconds at 600°C, the products are those formed from phenoxy and phenyl radicals. Phenoxy radicals are thought to be formed <u>via</u> an intermediate nitrite ester, which parallels the fragmentation processes observed in mass spectrometry; phenyl radicals may come from nitrosobenzene intermediates.(30)

When coal is pyrolyzed, gases are evolved. These gases include light hydrocarbons, carbon-, nitrogen-, and sulfur oxides, hydrogen sulfides, molecular hydrogen, ammonia and others. Gas evolution takes place during all three phases of pyrolysis. Below 350°C, evolved gases come mainly from the capillary system where they have been trapped during coalification or exposure to the atmosphere. In the 350 to 550°C range, gases are evolved as the matrix starts to break up. Decarboxylations take place in low-rank coals, generating CO_2. Reactions like those pictures in Figure 5 can generate CO and H_2.(4) In this temperature range, dehydroxylations can form H_2O and dealkylations can lead to the formation of methane and ethane.(22)

Above 550°C, in the secondary degasification phase, numerous reactions take place; some of these reactions take place as gas-solid reactions. Still others take place within the coal itself as rings begin to rupture, forming H_2 and CO (from hetero-oxygens). Still other reactions take place in the gas phase. These reactions are listed in Table 3, along with some of the reaction enthalpies. Exothermic reactions are not favored in an environment of high heat, but they do take place, putting still more energy into the system.

While the subject of this paper is coal science and not mathematics, two mathematical techniques were integral parts of this study; therefore, a discussion of these techniques is appropriate.

When an investigator wishes to examine the effects of varying several independent variables upon a dependent variable, he must carry out a certain number of experiments before he can see the true effects of his independent variables. In this paper, five independent parameters were examined: level of nitration, sample mass, initial helium pressure, time of reaction, and temperature of reaction. These variables were varied over three levels each (see Table 4)). In order to get an accurate estimate of the effect of these independent parameters on the dependent variables studied, 5^3 or 125 experiments would have had to have been run. Approximately six months would have been required to complete this number of experiments.

TABLE 3

Typical Secondary Degasification Phase Reactions

Gas-Solid Reactions:[a]	Enthalpy of Rxn.[b](31)
$C^b + O_2 \longrightarrow CO_2$	-393.5
$2C + O_2 \longrightarrow 2\ CO$	-221.
$C + 2H_2 \longrightarrow CH_4$	91.6
$C + CO_2 \longrightarrow 2CO$	172.5
$C + H_2O \longrightarrow CO + H_2$	131.3
Gas Phase Reactions:	
$2CO + O_2 \longrightarrow 2CO_2$	-566.0
$CO + H_2O \longrightarrow CO_2 + H_2$	-41.2
$CO + 3H_2 \longrightarrow CH_4 + H_2O$	-56.4
$CH_4 + 3/2O_2 \longrightarrow CO + 2H_2O$	-669
Hydrocarbons + $O_2 \longrightarrow CO + H_2O$	highly exothermic
Higher hydrocarbons ⟶ Lower Hydrocarbons + C(s)	
Unsaturated Hydrocarbons + H_2 ⟶ Saturated Hydrocarbons	
Unsaturated Hydrocarbons ⟶ Polymers	

a = From Reference 22.

b = All values in kilojoules.

c = Refers to activated carbon in the char.

TABLE 4

Independent Parameters Investigated in this Research and the Levels of Study

Independent Parameter	Levels
Sample Mass	1, 3, 5, gr
Initial Pressure	0, 500, 1000 psig
Soak Time	0.5, 1.5, 2.5 hrs.
Soak Temperature	250, 425, 600°C
Level of Nitration	0, 2.48, 3.56% Added N

A convenient, labor-saving device is available in a mathematical tool called Incomplete Block Experimental Design. Essentially, for n independent variables with given levels, an n-dimentional space is generated. The surface points and the center point of this space are taken from the given levels. These points translate into the minimum number of experiments necessary to determine the effects of changing the independent parameters upon a dependent quantity.

Thus, a 5^3 experiment block can be reduced to 22 experiments while still obtaining a reasonable idea of the importance of each parameter, for example upon the yield of tar from a coal pyrolysis. The key disadvantage to this technique is that, since at least two variables are changed from experiment to experiment, regression analysis must be used to interpret the data.

Regression analysis is a statistical technique through which one can relate a dependent variable and a set of independent or predictor variables. Regression analysis can be used either as a descriptive tool or as an inferential tool. When used as a descriptive tool, regression analysis does the following: One, it helps find the best prediction equation and evaluate its accuracy; two, it helps control other confounding factors in order to evaluate the contribution of a specific variable or set of variables; and three, the tool helps to provide explanations of seemingly complex relationships. When used as an inferential tool, regression analysis indicates relationships in a population based on the sample data.(32)

Regression analysis has the disadvantage of being complex and, to a non-statistician, extremely difficult to understand. Use of a computer is required, and the proper functions of the independent parameters must be selected for regression analysis. One must also recognize that regression analysis is predictive but does not necessarily predict accurately for a given experiment. It is, however, a great time-saver once its limits are understood.

In this research, regression analysis has been used as a descriptive tool to evaluate the contribution of soak time, sample mass, pyrolysis temperature, residence time, and level of nitration and initial pressure on given dependent parameters. The relationships between the five investigated parameters and the pyrolysis yields are complex, and regression analysis helps sort out the main effects from the trivial contributions of different factors.

CHAPTER III

EXPERIMENTAL

A. Instrumentation and Reagents

The base coal used for these experiments was a lignite from the Hagel Seam, Mercer County, North Dakota. The ultimate analysis of the coal is found in Table 6 in Chapter 4.

The coal was originally riffled on a Gisson Mini-Splitter. Later rifflings were carried out using a Brikman rotary splitter.

Lignite samples and fresh Soxhlet thimbles were dried in a National Appliance Company model 5831 vacuum oven.

Nitrosonium salts for lignite nitrations were supplied by Ozark-Mahoney Chemical Company. Reagent-grade nitromethane, used as a solvent in lignite nitrations, was supplied by either J. T. Baker Chemical Company or Fischer Chemical Company.

The computer program which generated the experimental design for this investigation is entitled COED, for Computer-Optimized Experimental Design. Access to this program was supplied as a service by Compuserve, Incorporated, Suite 1007, 1300 East Ninth Street, Cleveland, Ohio, 44114.

The pyrolysis reactors were Parr 71 milliliter model 58 HD high-pressure and high-temperature bombs. These bombs were constructed of either inconel or 3/16 stainless steel and are pictured in Figure 6. These bombs were modified with Swagelok and Whitey fittings supplied by Abbott Valve and Fitting of Solon, Ohio. Figure 7 shows the modifications used on the bombs.

Weighings, except for those carried out during the ashing procedure,were carried out on a Sartorius 1213 MP electronic balance. Weighings carried out during the ashing procedure were made on a Kahn TA 4100 electronic balance.

Gas samples were taken using a Whitey 304L-HDF4-150 150 ml. gas sample bomb, fitted as shown in Figure 7. Gas samples were analyzed on a Varian 5700 gas chromatograph with a 100/120 Carbosieve S-II column and a thermocouple detector. A 1 ml. injection volume was used. The column was held at 55°C for seven minutes, then raised to 150°C at a rate of 15°C/minute, where it was held for 22 minutes. Response factors were calculated using standard gas mixtures prepared by Matheson, Coleman and Bell.

Ammonium bicarbonate crystals were analyzed on an Analect RAM 50 infrared spectrometer and on a Phillips Manual XRD X-ray diffraction spectrometer with a K-α radiation source.

The n-hexane used for oil extraction was HPLC grade, either used "as is" or distilled over $CaCl_2$ before use. The toluene used for asphaltene extraction was reagent grade and was used either "as is" or distilled over P_2O_5 before use. Preasphaltenes were extracted with tetrahydrofuran (THF) which contained about 0.7 mole-percent water.

Elemental analysis of the residual coal was carried out on a LECO CHN 600 carbon hydrogen nitrogen analyzer, as well

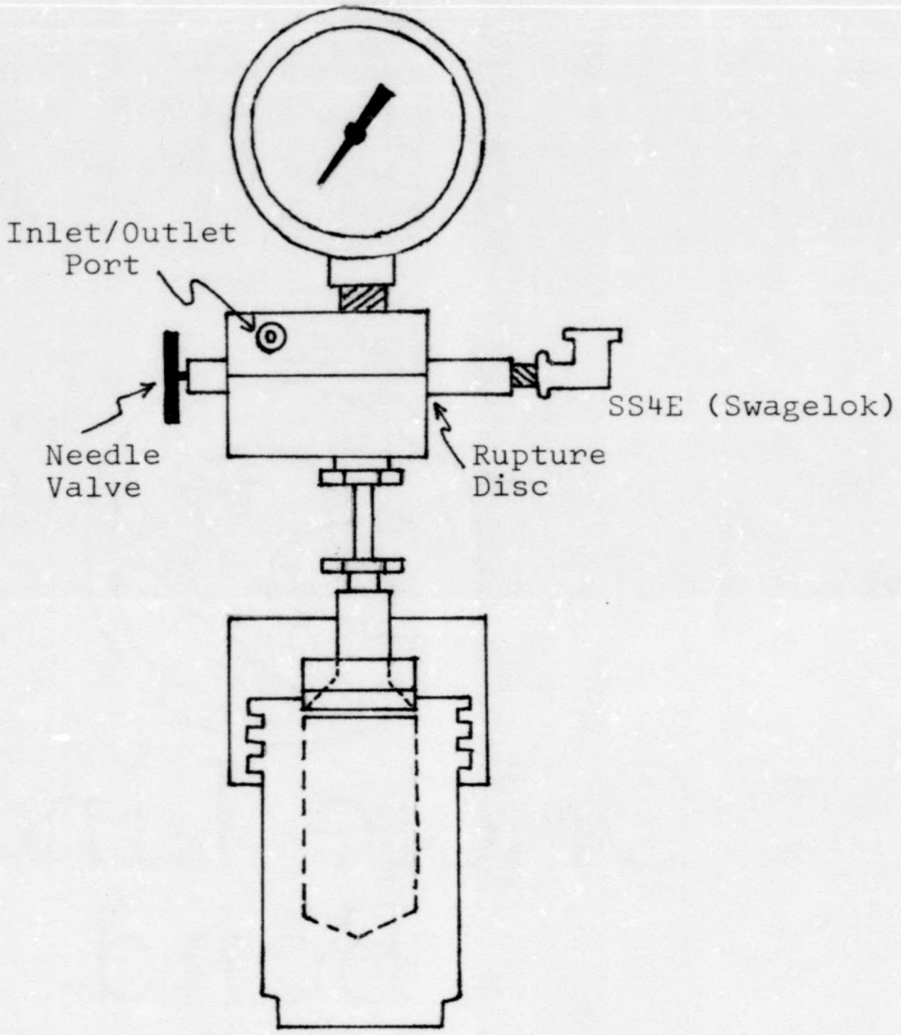


Figure 6. The Parr 58 HD 71 ml. Reactor.

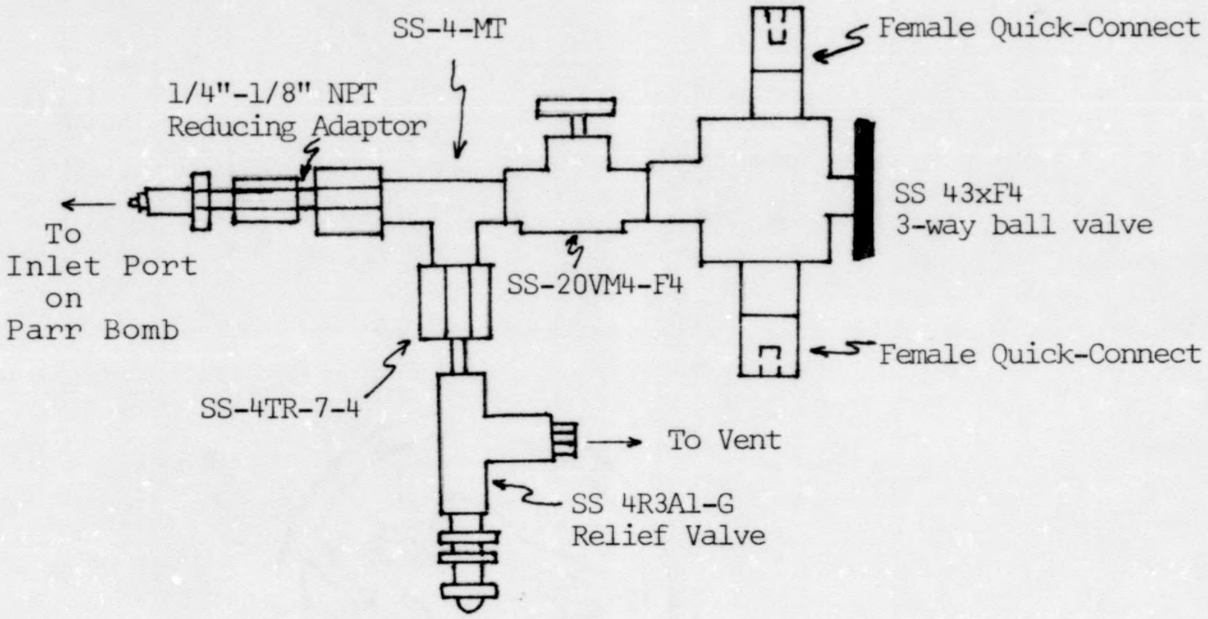


Figure 7. Modifications to the Parr 58 HD Reactor used in this research.

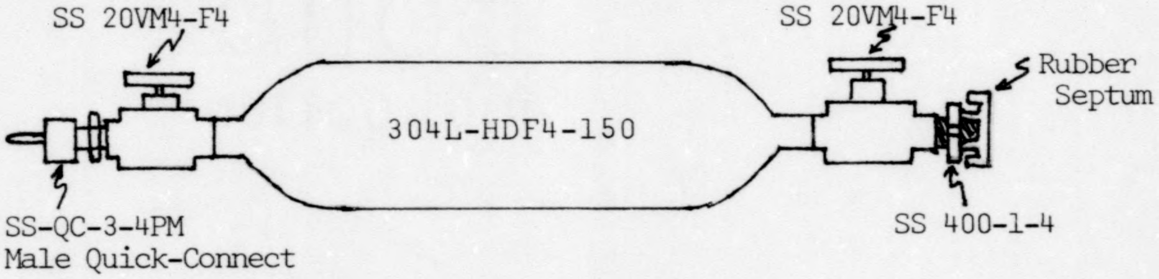


Figure 8. Whitey Gas Sampling Bomb with Modifications.

as on a LECO SC 132 sulfur analyzer. Ashings were done in a Thermolyne muffle furnace.

Data analysis was done using SAS, a regression analysis package provided by Statistical Analysis Systems Institute, Incorporated, of Cary, North Caroline. The program was run with the help of the Academic Computing and Research Service of Western Kentucky University of Bowling Green, Kentucky.

B. Procedure

A sample lignite was taken from a barrel containing run-of-the-mine coal. The coal was passed once through a chipmunk grinder. The ground coal was sifted so as to obtain about 400 grams of -65 mesh lignite. The coal was then riffled into four splits using the Gilson Mini-Splitter. One lot was discarded, and the other three were dried over-night at 105°C under a vacuum.

Two of the three dried lots were subjected separately to nitration. The third lot, labeled 10821-38A, was allowed to remain untreated for use as a control. Nitration was carried out by adding NO_2PF_6 to nitromethane, followed by the addition of lignite. Both lots of the treated coal were nitrated for 24 hours, batch 10821-38B at 0°C and batch 10821-38C at 25°C.

The three individual lots of coal were riffled down to sample sizes of about 1, 3 and 5 grams using the Brinkman rotary splitter to ensure equivalence within each coal lot so that a given experiment could be repeated.

The conditions used for each experiment were decided upon by the COED package supplied by Compuserve, Inc. The conditions were decided upon on the basis of the independent parameters which were chosen for study in this investigation. The parameters studied and the levels of each are listed in Table 4. The series of experiments actually carried out are listed in Table 5. Experiments additional to those generated by COED were carried out to obtain more data and ensure repeatability.

Extractions of the untreated and treated coals were done to compare with the extractions of the pyrolysis chars. In order to include the extraction data (and the ultimate analysis of the residuals), the extractions of the original coals were treated as pyrolysis reactions at room temperature (23°C), 0 psig pressure, 0 hours soak time, and were assumed to have a volatile yield of 0 percent. They are labeled Experiments 24, 25 and 26 in Table 5. Volatile yields were treated as missing data in the regression analysis, as were the contents of the pyrolysis off-gas.

The coal was pyrolyzed by adding the desired sample of lignite to the clean, dry Parr bomb. The bomb was sealed and flushed two to three times with helium. The bomb was then pressurized with helium and placed in the ceramic furnace. The furnace was allowed to heat at its natural rate to the desired soak temperature. The overall rate of heating to 250°C from ambient temperature was about 23°C/minute, to 425°C the rate was about 15°C/minute.

TABLE 5

Experimental Conditions for the Pyrolysis Runs Carried out in this Research

Expt. No.[a]	% Added Nitrogen	Weight[b]	Press.[c]	Temp.[d]	Time[e]
1	0	5.00	1000	250	0.5
2	0	5.01	0	600	0.5
2'	0	4.80	0	600	0.5
3	0	5.00	0	250	2.5
4	3.56	1.00	1000	425	1.5
4'	3.56	0.89	1000	425	1.5
4"	3.56	0.90	1000	425	1.5
5	3.56	5.00	1000	600	0.5
5'	3.56	4.15	1000	600	0.5
6	0	1.02	500	425	2.5
6'	0	1.03	500	425	2.5
7	0	0.97	500	250	1.5
8[f]	2.48	2.73	500	425	1.5
8'	2.48	2.70	500	425	1.5
8"	2.48	2.70	500	425	1.5
9	3.56	1.02	0	250	0.5
10	2.48	1.02	1000	250	0.5
11	0	3.05	1000	250	0.5
12	3.56	4.55	1000	250	2.5
13	3.56	4.60	0	425	1.5
14	0	1.00	0	425	1.5
14'	0	0.87	0	425	1.5
15	3.56	1.00	0	600	2.5
16	0	4.75	1000	600	2.5
17	0	3.04	1000	600	1.5
18	3.56	4.55	500	250	0.5
19	2.48	5.04	0	600	2.5
20	2.48	2.66	0	250	1.5
21	2.48	4.75	1000	250	1.5
22	3.56	0.97	500	600	0.5
23[g]	0	1.04	1000	600	1.0
24[g]	0	1.10	0	23	0
25[g]	0	2.37	0	23	0
26[g]	0	1.98	0	23	0

a = Experiments marked with primes or double primes are repeats of experiments in the original 22-experiment experimental design.

b = Sample Mass in Grams.

c = Pressure in psig.

d = Temperature in degrees Centigrade.

e = Time in hours.

f = This is the midpoint experiment.

g = This experiment was added to the original experimental design.

Once the furnace reached the desired temperature, it was held there for the desired soak time. The bomb was then removed and allowed to cool slowly overnight.

Before the cooled bomb was opened, a gas sample was taken using the evacuated Whitey gas sampling bomb shown in Figure 6. From this sample bomb, 1 ml. of gas was removed with a gas-tight syringe and was analyzed with the Varian 5700 gas chromatograph. The Parr reactor was then opened, any extraneous solids were removed, and then the coal was taken out and weighed on the Sartorius balance.

The coal was then placed in a dry, pre-weighed Soxhlet thimble and extracted overnight with n-hexane. After the extraction, the thimble was dried for four hours at 100°C under a vacuum; following the drying, the thimble with the coal was weighed and any weight change was noted. The coal and thimble were then placed again in a Soxhlet extractor and were extracted overnight with toluene, and dried and weighed. The coal was similarly extracted with THF overnight; following the drying and weighing, the lignite was removed from the thimble and split into two lots with the Gilson Mini-Splitter.

One split of the lignate residual was analyzed for carbon, hydrogen, nitrogen and sulfur content. The other split was ashed. Ashings were carried out by heating the residual to 750°C and soaking it overnight then weighing the ash on the Kahn TA 4100 balance.

Once all the data were collected and tabulated, the experimental conditions and the collected data were entered into the SAS package for regression analysis. The forward and backward stepwise options were utilized in the data analysis. The former enters, one at a time, the most statistically significant variables into the predictive equation until no remaining variables are significant. The latter enters all the variables and removes, one at a time, all statistically insignificant variables in order of increasing significance. The predictive equations were then graphed by the SAS package.

CHAPTER IV

RESULTS

The base lignite used in this study is a part of the Pennsylvania State University data base and has been extensively characterized by the university. The sample used in this research, as well as the nitrated splits, was subjected to elemental analysis. The results are found in Table 6.

TABLE 6

Ultimate Analyses of Coals Used in this Research

	10821-38A[a]	10821-38B[a]	10821-38C[a]
% Carbon	60.22	58.08	56.12
% Hydrogen	4.57	4.07	3.62
% Nitrogen	1.22	3.36	4.17
% Sulfur	.86	0.73	.69
% Ash	8.61	4.01	3.6
% Oxygen	25	30	32

a = All values on a moisture-free basis.

The level of nitration was determined by the formula used in Equation 18

$$\frac{N'}{(C'/C)} - N = \%\ \text{Added Nitrogen} \qquad (18)$$

where N and C are the percentage of nitrogen and carbon in the untreated coal and N' and C' are the percentages of nitrogen and carbon in the untreated coal (on an ash free basis), and N' and C' are the percentages of nitrogen and carbon in the nitrated coal, also on an ash-free basis. Coal sample 10821-38B contains 2.48% added nitrogen, and coal sample 10821-38C contains 3.56% added nitrogen.

The added oxygen is computed in the same way as the added nitrogen. Coal 10821-38B has an added oxygen to added nitrogen ratio of 2.4; coal 10821-38C has an added oxygen to added nitrogen ratio of 2.5.

The added oxygen ratio is computed in a like fashion to the added nitrogen. The added oxygen-to-added nitrogen ratios are 2.4 and 2.5 (mole/mole) for coals 10821-38B and 10821-38C, respectively. Since the O/N ratio for a nitro group is 2.0, the samples apparently underwent some oxidation during the pretreatment.

Table 7 provides a compilation of the yields of volatile material, oils, asphaltenes, preasphaltenes, and residual char.

Table 8 contains the elemental analyses of the residual chars.

The results of the gas-chromatography analyses of the off-gases of the pyrolysis reactions are found in Table 9.

Table 10 contains the predictive equations generated by the SAS regression analysis program from the data in Tables 5, 7, 8, and 9. Table 10 also contains statistical data for each model euqtion.

Figure 9 is a graph of the percent volatiles yield versus temperature. This graph is generated from Equation 19 in Table 10.

TABLE 7

Percentages of Volatiles, Oils, Asphaltenes, Preasphaltenes and Chars

Exp. No.[a]	Vol. Yield[b]	% Oils[b]	%Asphaltenes[b]	% Preasphaltenes[b]	% Residual[b]
1	0.400	3.80	1.20	-1.00[c]	98.8
2	26.2	4.80	0	-0.02	70.9
2'	25.2	5.63	----[d]	-----	----
3	0.80	3.8	-1.00	0.40	96.6
4	21	7.00	0	-1.00	75.0
4'	19	6.00	0	-3.00	78.7
4"	23	7.00	----	-----	----
5	32.6	6.80	-0.40	0.200	60.4
5'	36.1	----	-----	-----	----
6	16	7.84	0.00	-0.98	77.5
6'	25	----	-----	-----	----
7	0.0	8.25	0.00	-2.06	95.9
8	----	----	0.37	-2.20	78.4
8'	18.9	4.07	0.370	-0.74	77.0
8"	15.6	5.56	0.370	-0.19	81.1
9	2.9	0.98	0	5.88	90.2
10	0.98	2.94	0	0	96.1
11	0	4.59	1.31	-3.28	97.0
12	5.05	3.74	-2.20	4.84	88.6
13	25.4	4.35	0.22	-1.09	71.1
14	16	4.00	3.00	-4.00	81.0
14'	14	8.05	3.45	-3.45	78.2
15	40	3.00	0	-3.00	60.0
16	35.8	1.68	1.05	-0.63	62.1
17	34.2	2.96	0	-1.64	64.5
18	1.10	1.98	0.88	2.42	96.0
19	33.7	6.35	0.198	-0.99	60.7
20	4.13	6.02	-0.38	1.88	88.3
21	3.37	3.16	0.42	-1.05	94.1
22	32	6.2	-1.0	-2.1	65
23	29.8	2.88	0.96	-0.96	69.2
24	----	4.55	0	0	95.5
25	----	3.80	-0.42	0.84	95.8
26	----	4.55	-0.51	-0.51	96.5

a = Experiment numbers correspond to Table 5.

b = All percentages are percent of the original sample weight.

c = Negative values indicate that the extracted coal adsorbed solvent during extraction.

d = Dashes indicate missing values.

TABLE 8

Ultimate Analyses of the Residual Chars

Expt. No.[a]	% C[b]	% H	% N	% S	% Ash	% O
1	59.74	4.45	1.19	0.83	10.07	23
2	74.10	3.36	1.53	1.09	16.2	3.75
2'	----[c]	----	----	----	----	----
3	60.60	4.50	1.24	0.89	8.33	24
4	70.67	3.45	3.93	0.76	4.33	17
4'	65.78	3.46	4.31	----	5.05	----
4"	-----	----	----	----	----	----
5	78.13	3.09	4.96	1.00	4.68	8.14
5'	-----	----	----	----	----	----
6	71.29	4.19	1.18	0.81	12.7	10
6'	-----	----	----	----	----	----
7	63.36	4.81	1.00	----	9.88	----
8	69.76	3.73	3.30	0.82	7.9	14
8'	69.47	3.80	3.48	0.84	5.17	17
8"	68.72	3.03	3.88	----	4.68	----
9	58.85	3.69	3.81	0.68	3.0	30
10	61.64	4.31	2.57	0.68	4.8	26
11	61.57	4.39	1.34	0.89	7.75	24
12	60.09	3.60	4.02	0.71	4.1	27
13	70.65	3.27	4.83	0.74	4.18	16
14	68.29	3.99	1.66	0.86	9.87	15
14'	-----	----	----	----	----	----
15	79.83	2.98	4.13	0.88	4.5	7.7
16	79.42	2.92	1.44	1.19	12.3	2.73
17	77.92	3.07	1.46	1.20	12.0	4.35
18	58.84	3.75	3.84	0.68	2.7	30
19	82.67	2.99	3.10	0.89	5.7	4.7
20	62.12	4.09	2.81	0.71	3.86	26
21	62.06	4.13	2.60	0.74	4.69	26
22	74.50	3.16	4.51	----	4.1	----
23	-----	----	----	----	----	----
24	-----	----	----	----	8.90	----
25	60.09	4.20	2.89	0.69	3.69	28
26	58.78	3.70	3.83	0.62	2.5	31

a = Experiment numbers correspond to Table 5.

b = All values in % of the char, moisture-free basis.

c = Dashes indicate missing values.

TABLE 9

GC Analysis of the Pyrolysis Off-Gases

Expt. No.	% H_2	% N_2	% CO	% CH_4	% CO_2	NH_3
1	0	0	0	0	0	No
2	----	----	----	----	----	No
2'	8.35	0	4.35	17.7	48.5	No
3	0	0	0	0	0	No
4	----	----	----	----	----	No
4'	0	0	0.220	0	0	No
4"	0	0	0	0	0	No
5	----	----	----	----	----	--
5'	0	0	0.525	0	7.69	Yes
6	----	----	----	----	----	No
6'	0	0	----	0	----	--
7	0	0	0	0	0	No
8	----	----	----	----	----	No
8'	0	0	0.620	0	5.69	No
8"	0	0	0.948	0	6.99	No
9	0	0	0	0	0	No
10	0	0	0	0	0	No
11	0	0	0	0	0	No
12	0	0	0	0	0	No
13	0	3.12	10.4	1.26	61.7	Yes
14	0	0	1.60	0.695	11.4	No
14'	0	0	1.52	0	9.73	No
15	6.06	0.927	4.54	7.96	38.3	Yes
16	0	0	0	6.39	9.37	No
17	0	0	0.241	3.26	5.54	No
18	0	0	0	0	0	No
19	2.67	2.27	5.28	22.1	55.6	Yes
20	0	0	0.876	0	10.4	No
21	0	0	0	0	0	No
22	0	0	0.305	0	0	No
23	----	----	----	----	----	No
24	----	----	----	----	----	No
25	----	----	----	----	----	No
26	----	----	----	----	----	No

a = Experiment numbers correspond to Table 5.

b = All values in volume-percent.

c = Ammonia not noted on the GC, but detected by smell and the presence of ammonium bicarbonate crystals.

d = Dashes indicate missing values.

TABLE 10

Predictive Equations for the Dependent Variables Examined in this Research

Equation	Correlation Coef.
(19) $\%VY = -1.70 + 9.9 \times 10^{-5}(Tm)^2$	0.9
(20) $\%Res. = 98 - 9.7 \times 10^{-5}(Tm)^2$	0.95
(21) $\%C = 58 + 5.6 \times 10^{-5}(Tm)^2$	0.96
(22) $\%H = 4.6 - 1.6 \times 10^{-1}(N) - 3.4 \times 10^{-6}(Tm)^2$	0.90
(23) $\%N = 1.3 + 7.9 \times 10^{-1}(N)$	0.96
(24) $\%S = 7.9 \times 10^{-1} - 4.5 \times 10^{-3}(N) + 8.7 \times 10^{-7}(Tm)^2$	0.94
(25) $\%Ash = 8.4 - 2.0(N) + 6.6 \times 10^{-3}(Tm)$	0.94
(26) $\%O = 30 - 7.0 \times 10^{-5}(Tm)^2$	0.96
(27) $\%CO_2 = -9.2 + 3.7(Wt) + 3.5 \times 10^{-2} - 0.02(P)$	0.81
(28) $\%CH_4 = -1.8 + 5.5 \times 10^{-2}(Tm)^2 + 2.1 \times 10^{-1}(Wt)^2 - 4.5 \times 10^{-3}(P)$	
(29) $\%Oils = 4.7$	0.00
(30) $\%H_2 = 1.0 \times 10^{-1} - 1.6 \times 10^{-3}(P) + 7.9 \times 10^{-6}(Tm)^2$	0.62
(31) $\%N_2 = -4.1 \times 10^{-1} + 1.4 \times 10^{-1}(N) - 7.9 \times 10^{-6}(P) + 1.1 \times 10^{-3}(Tm)$	0.64
(32) $\%CO = 6.5 \times 10^{-1} + 3.9 \times 10^{-1} - 2.9 \times 10^{-1}(P) + 5.8 \times 10^{-3}(Tm)$	0.70

Tm = Temperature

Wt = Sample Mass

P = Pressure

N = Percent added nitrogen

Figure 10 is a plot of the percent residual yield against temperature. This plot is generated from Equation 20 in Table 10.

Figure 11 is a plot of the percent carbon in the residual versus temperature. The graph in this figure is generated from Equation 21 in Table 10.

Figure 12 is a contour plot of the percent hydrogen in the char versus percent nitration and temperature. Figures 13, 14 and 15 are graphs of the percent hydrogen versus temperature at constant nitration levels of 0, 2.48 and 3.56% added nitrogen, respectively. Figure 9 and the other computer-generated graphs in this chapter may have an axis labeled "Alt." The abbreviation "Alt" (for "alteration") was used as a sort of pseudonym for the process of nitration, which was still proprietary at the time of the writing of this paper. Figure 12 through 15 are generated from Equation 22 in Table 10.

Figure 16 is a graph of the percent nitrogen in the residual char against the percent nitration and is generated from Equation 23 in Table 10.

Figure 17 is a contour plot of the percent sulfur in the residual char versus the percent nitration and temperature. Figures 18, 19 and 20 are graphs of the percent sulfur versus temperature at 0, 2.48 and 3.56% added nitrogen, respectively. Figures 17, 18, 19 and 20 are generated from Equation 24 in Table 10.

Figure 21 is a contour graph of the percent ash in the char against temperature and percent added nitrogen.

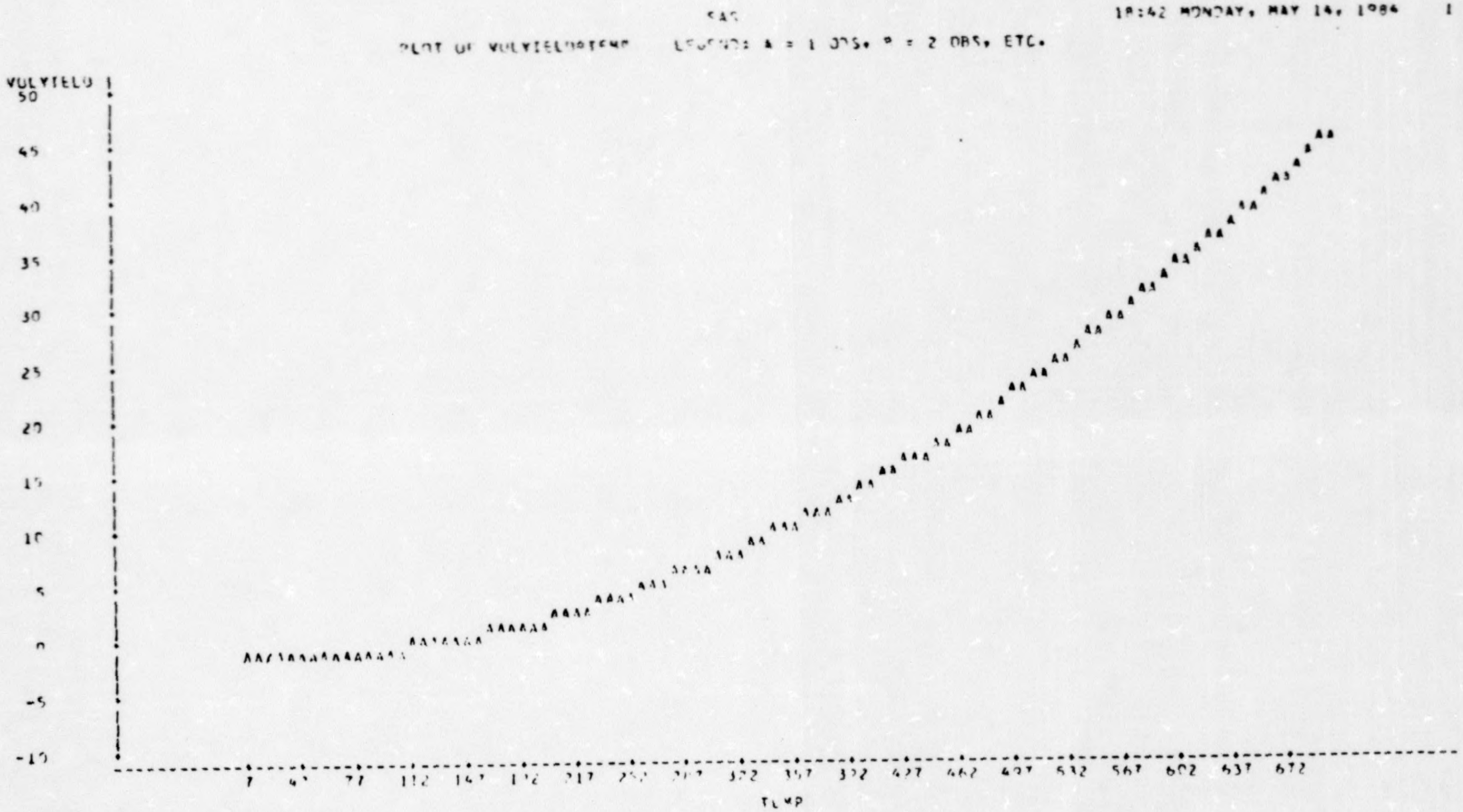


Figure 9. Percent volatiles yield versus temperature.

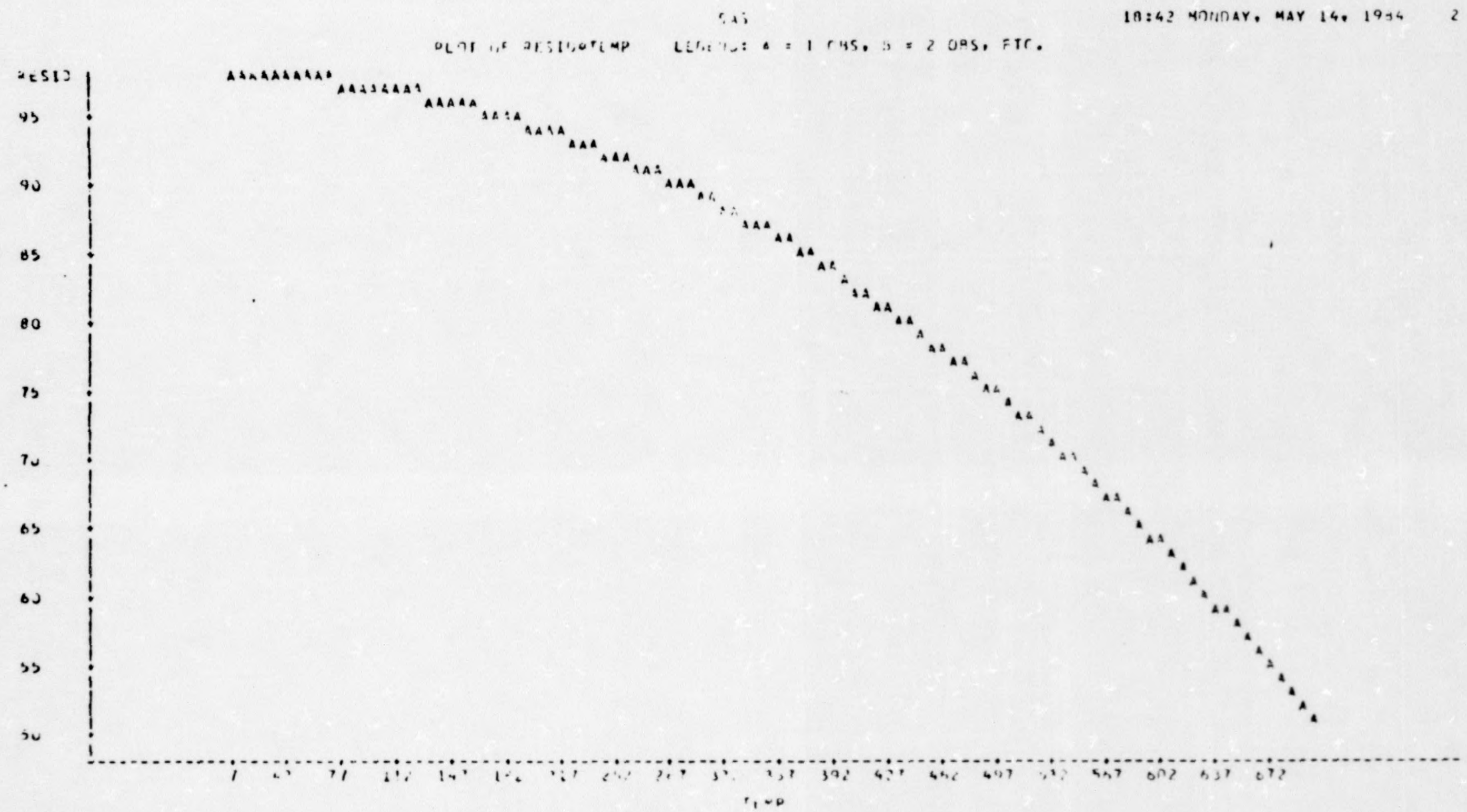


Figure 10. Percent residual versus temperature.

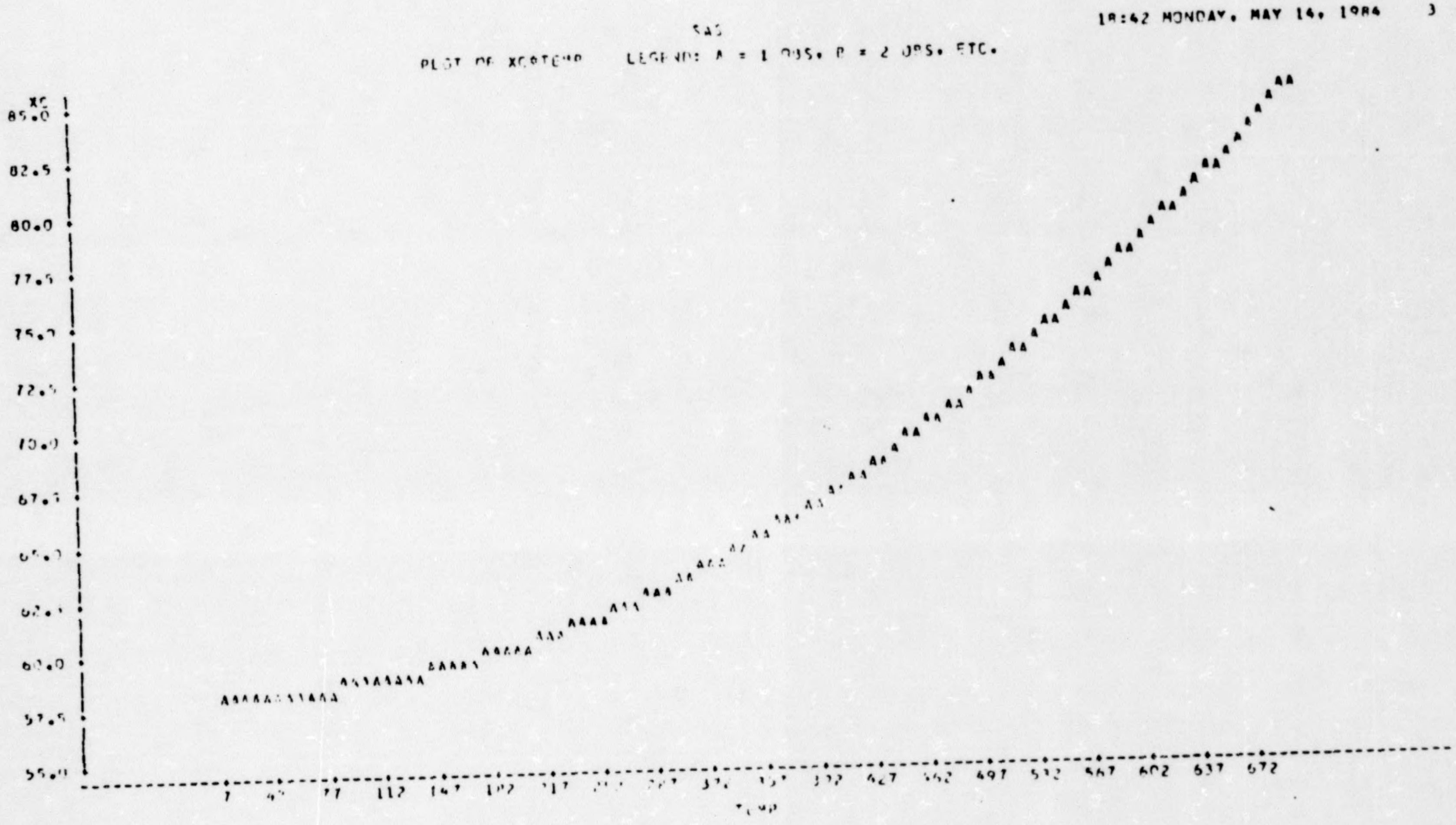


Figure 11. Percent carbon in the residual versus temperature.

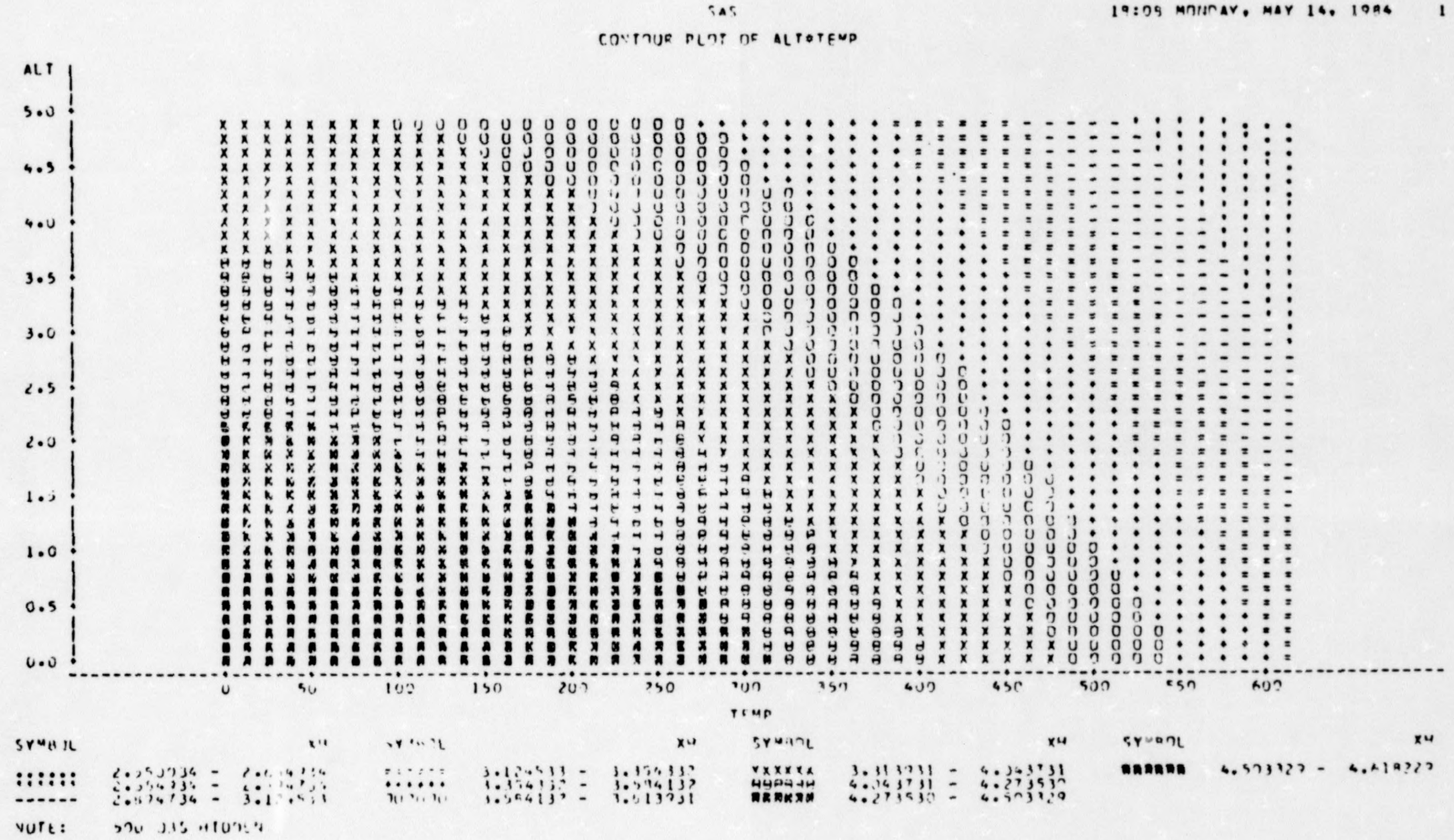


Figure 12. Percent hydrogen in the residual versus temperature and nitration.

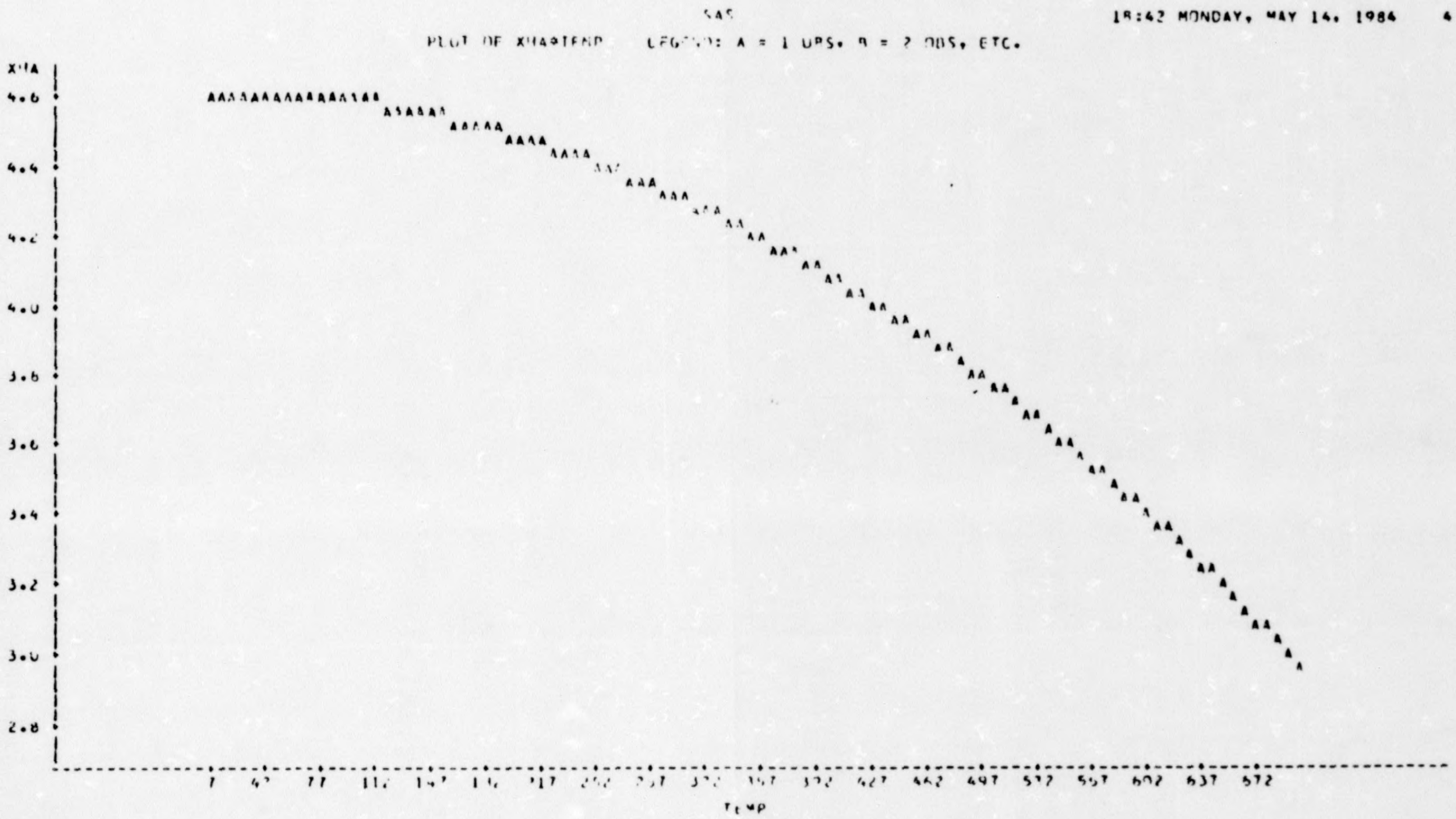


Figure 13. Percent hydrogen in the residual versus temperature at 0% added nitrogen.

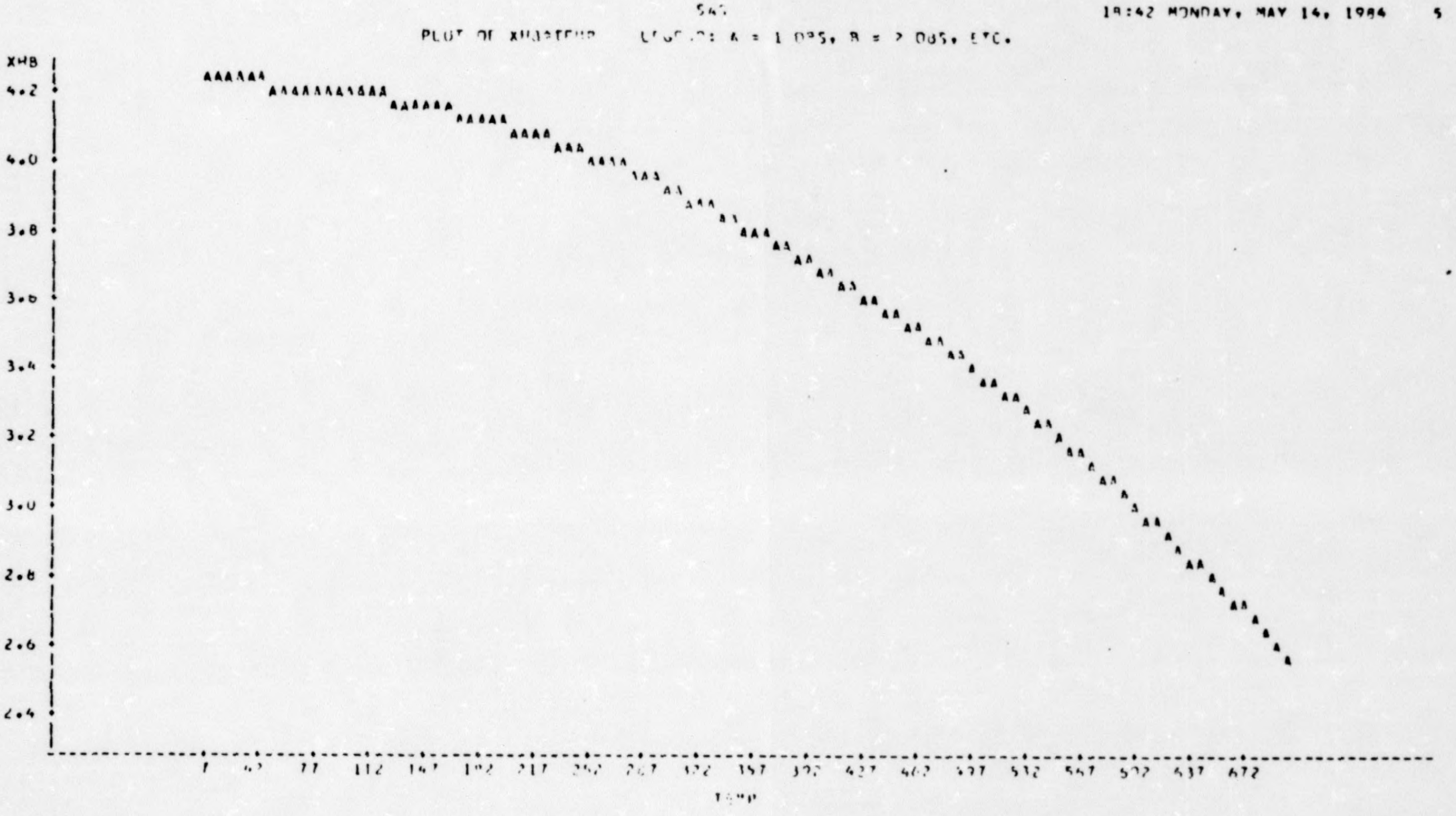


Figure 14. Percent hydrogen in the residual versus temperature at 3.44% added nitrogen.

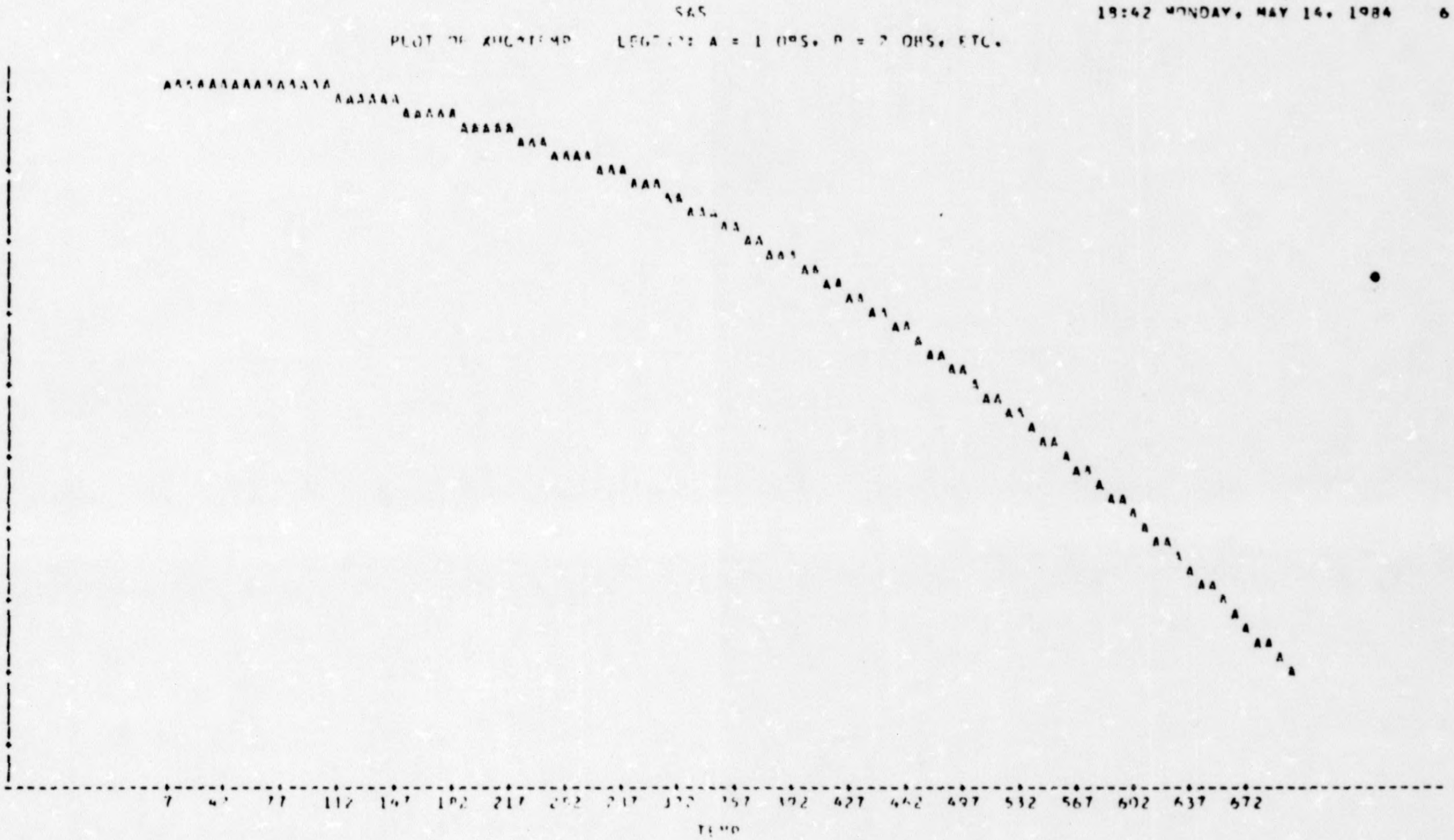


Figure 15. Percent hydrogen in the residual versus temperature at 3.44% added nitrogen.

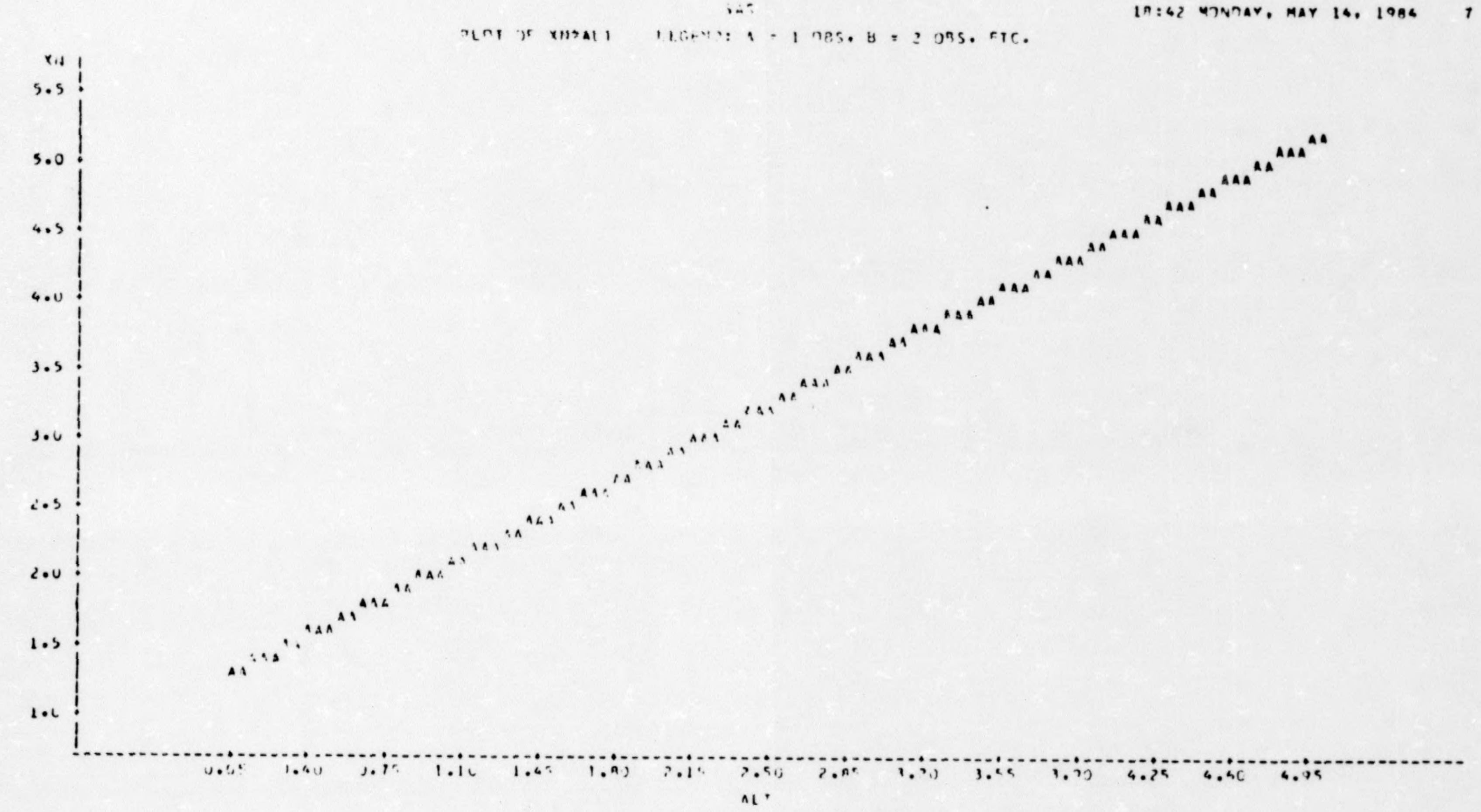


Figure 16. Percent nitrogen in the residual versus percent added nitrogen.

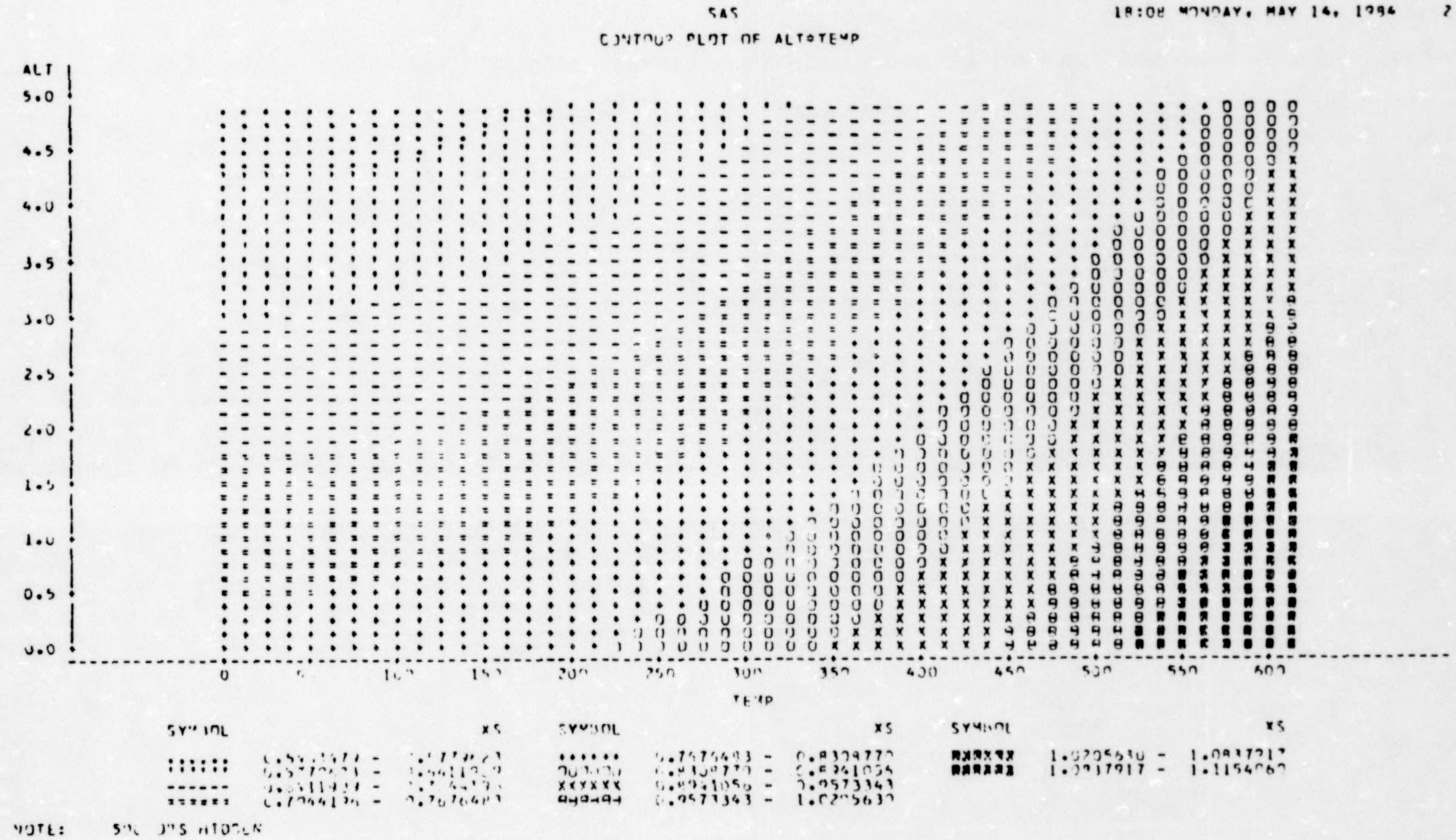


Figure 17. Percent sulfur in the residual versus temperature and percent added nitrogen.

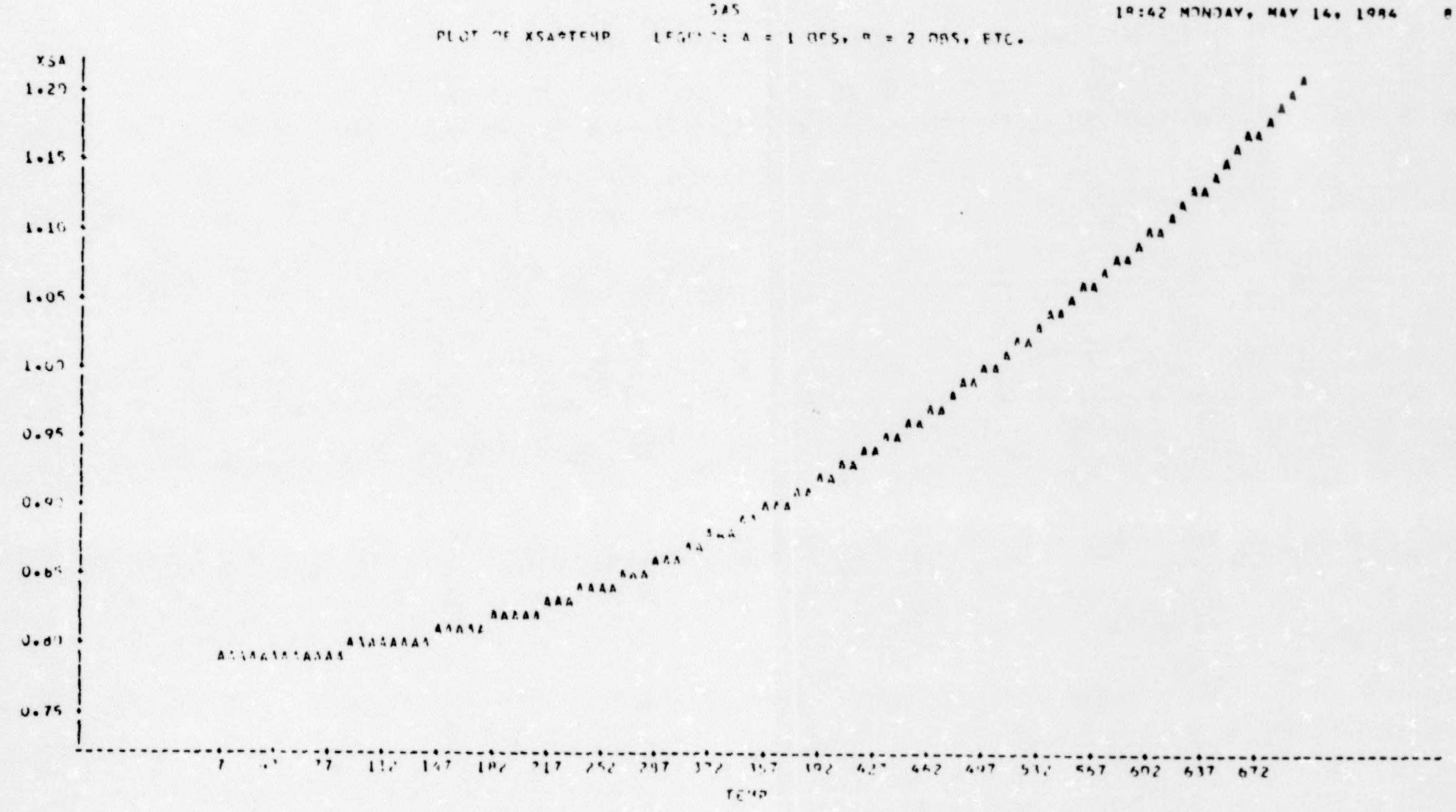


Figure 18. Percent sulfur in the residual versus temperature at 0% added nitrogen.

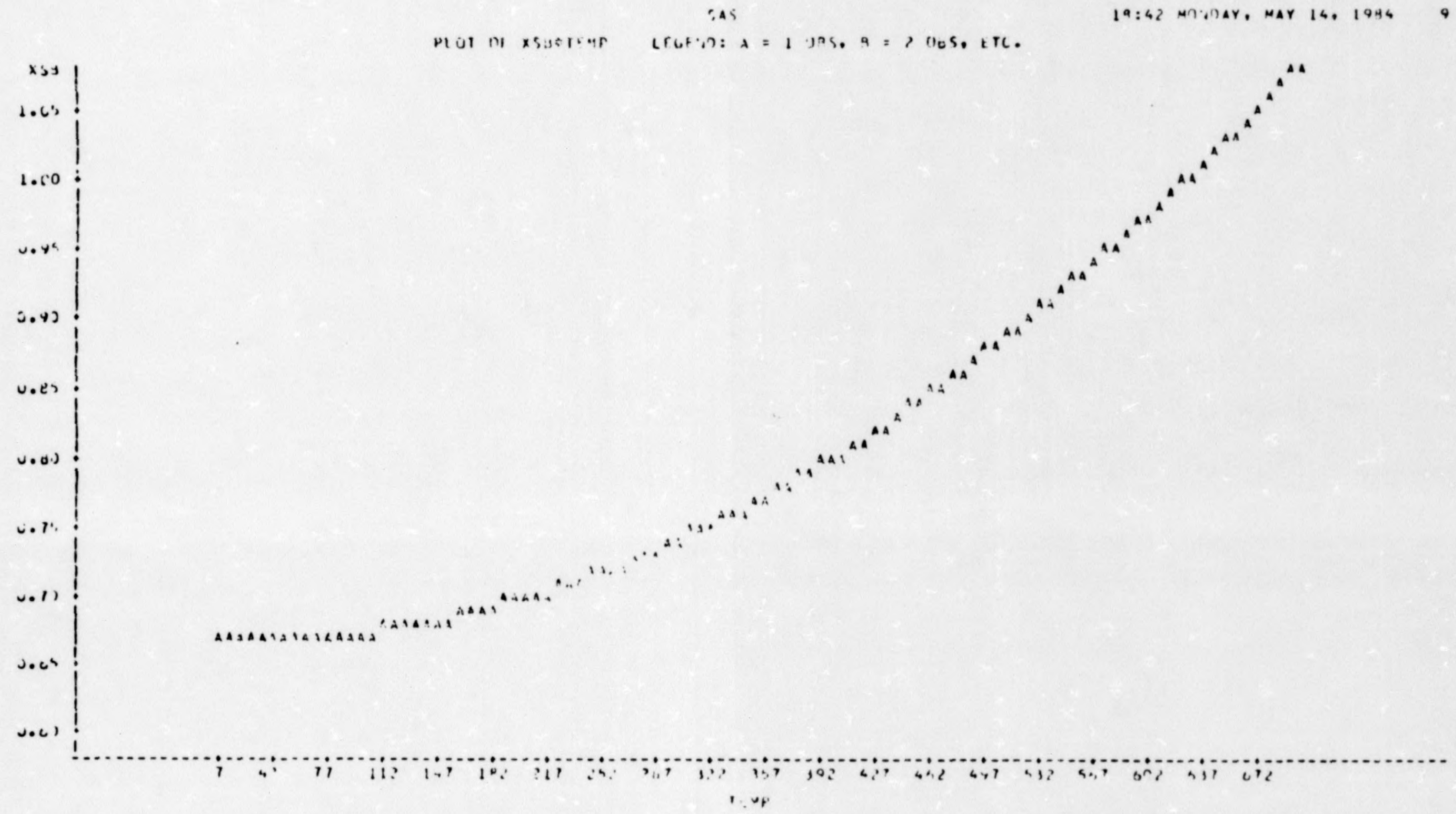


Figure 19. Percent sulfur in the residual versus temperature at 2.39% added nitrogen.

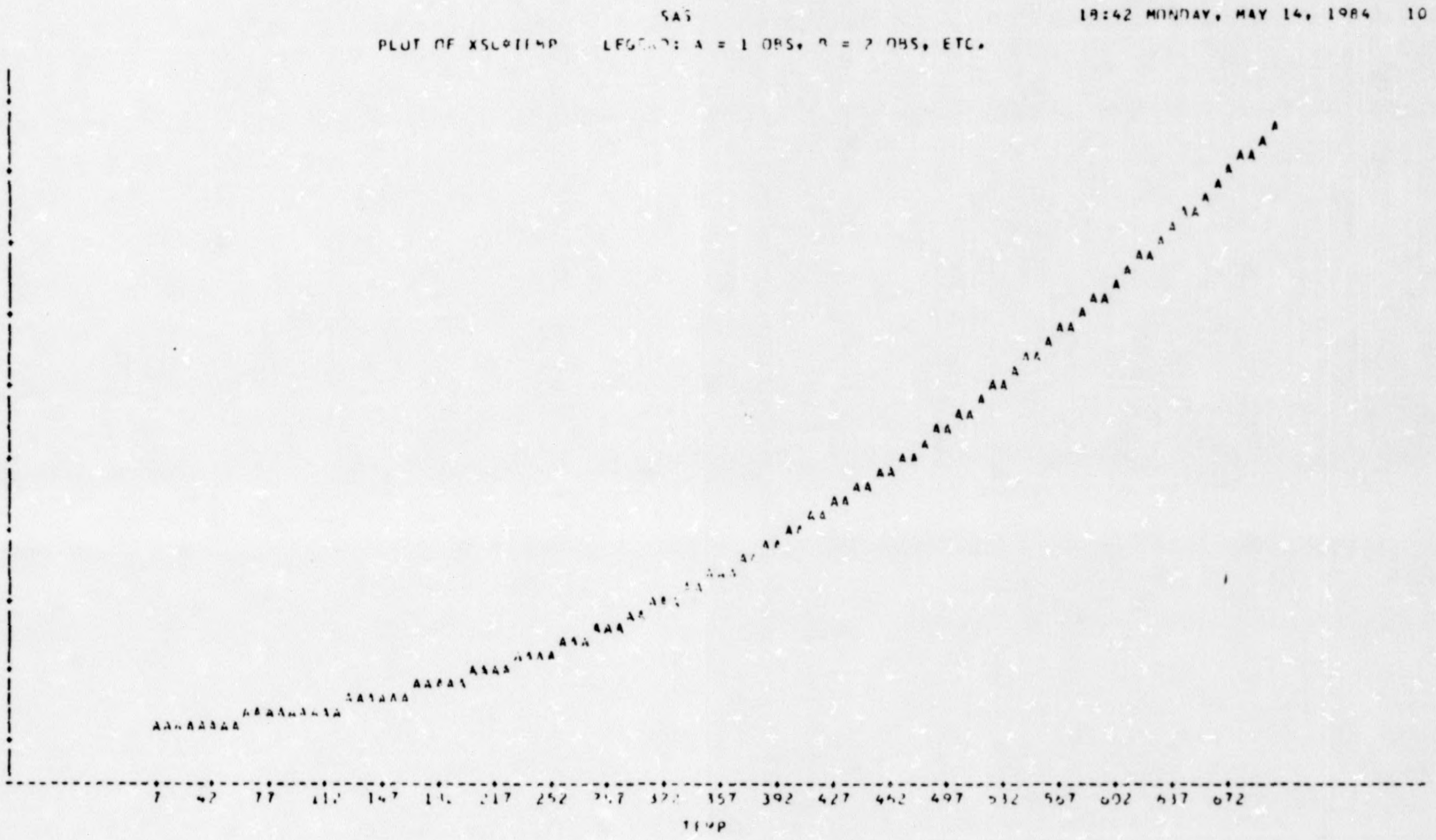


Figure 20. Percent sulfur in the residual versus temperature at 3.44% added nitrogen.

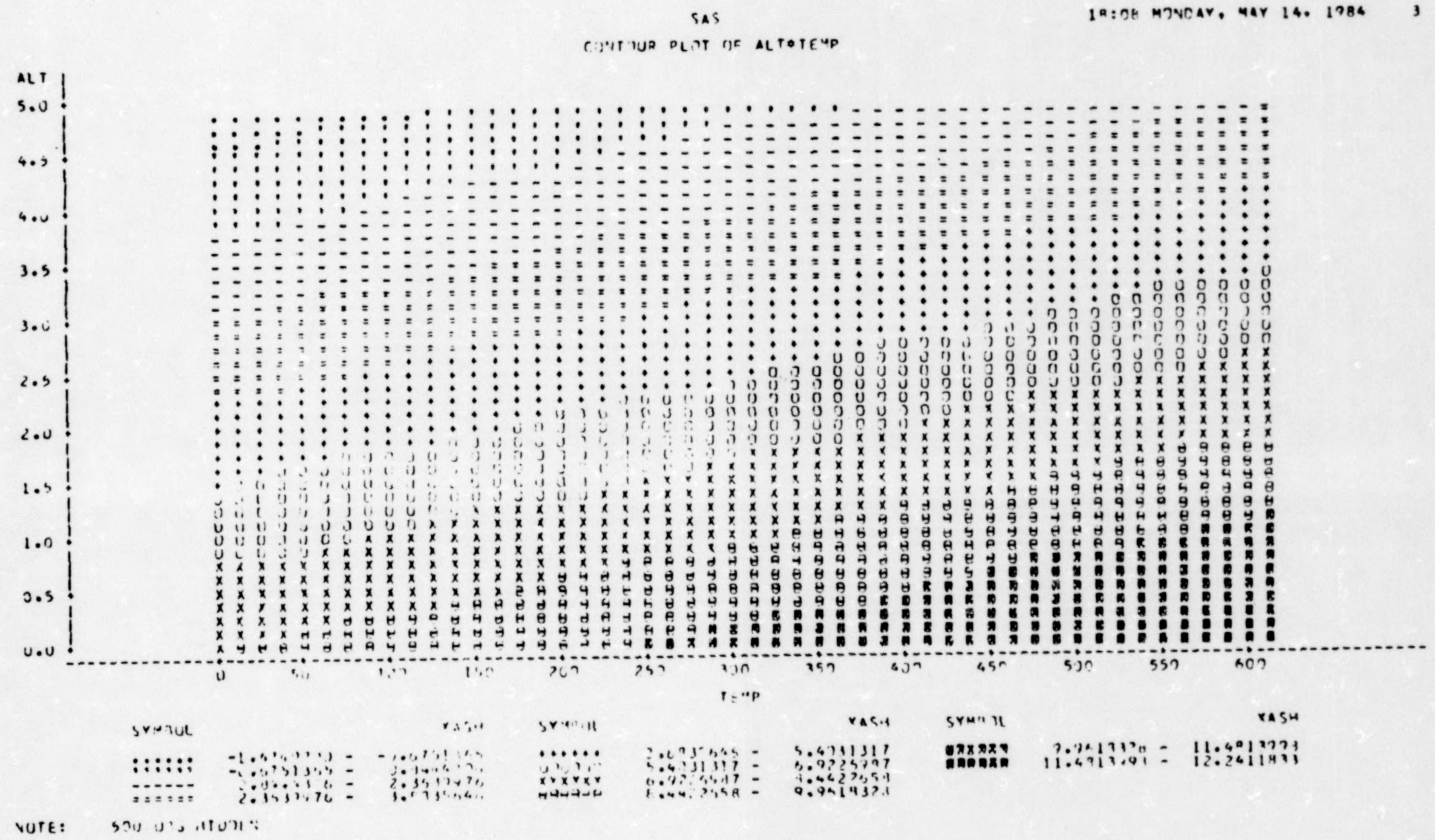


Figure 21. Percent ash in the residual versus temperature and percent added nitrogen.

Figures 22, 23 and 24 are plots of the percent ash in the residual versus percent added nitrogen at constant pyrolysis temperatures of 250, 425 and 600°C, respectively. Figures 21, 22, 23 and 24 are generated from Equation 25 in Table 10.

Figure 25 is a plot of the percent oxygen in the char against temperature, and is generated from Equation 26 in Table 10.

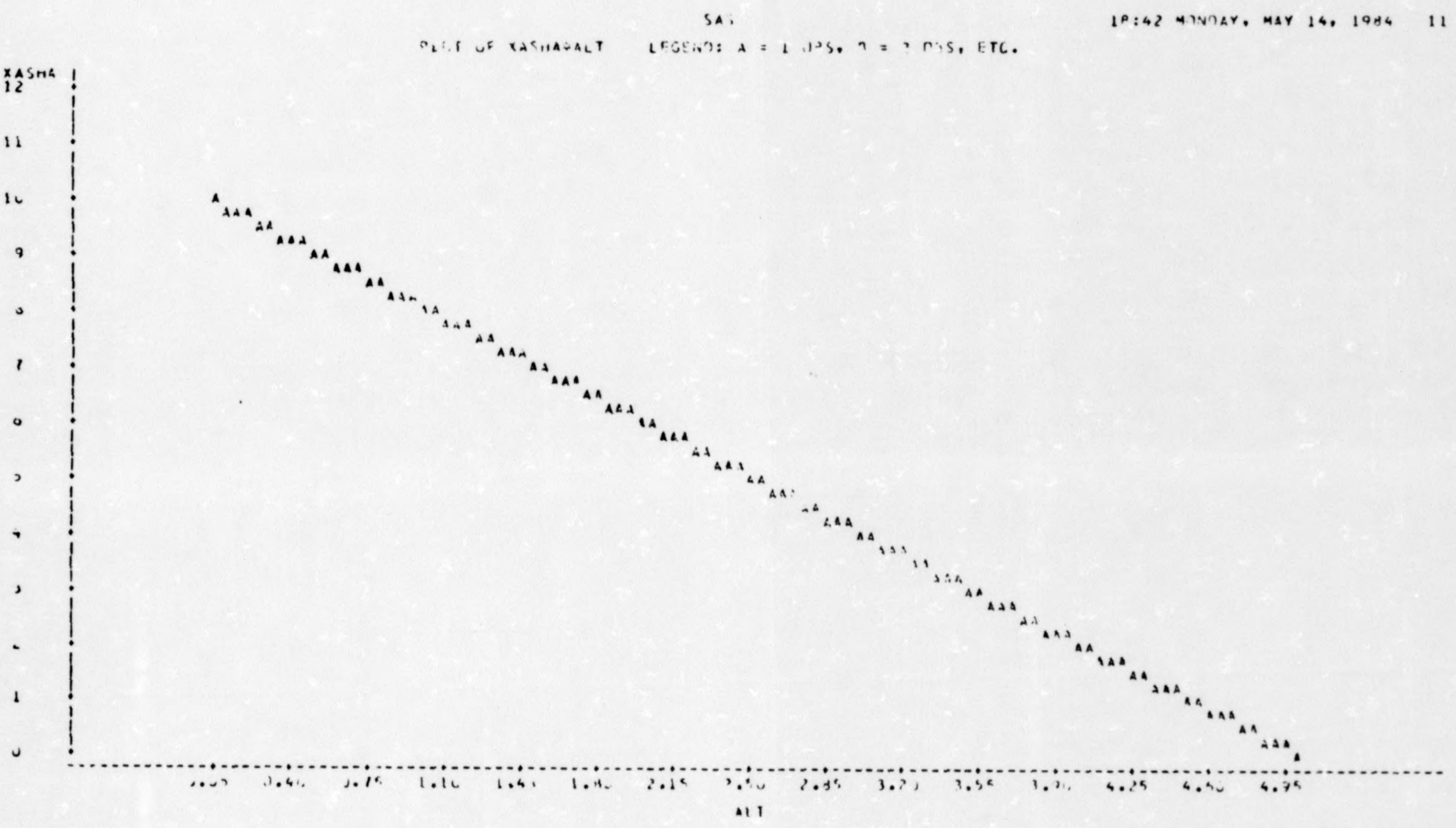


Figure 22. Percent ash in the residual versus percent added nitrogen at 250°C.

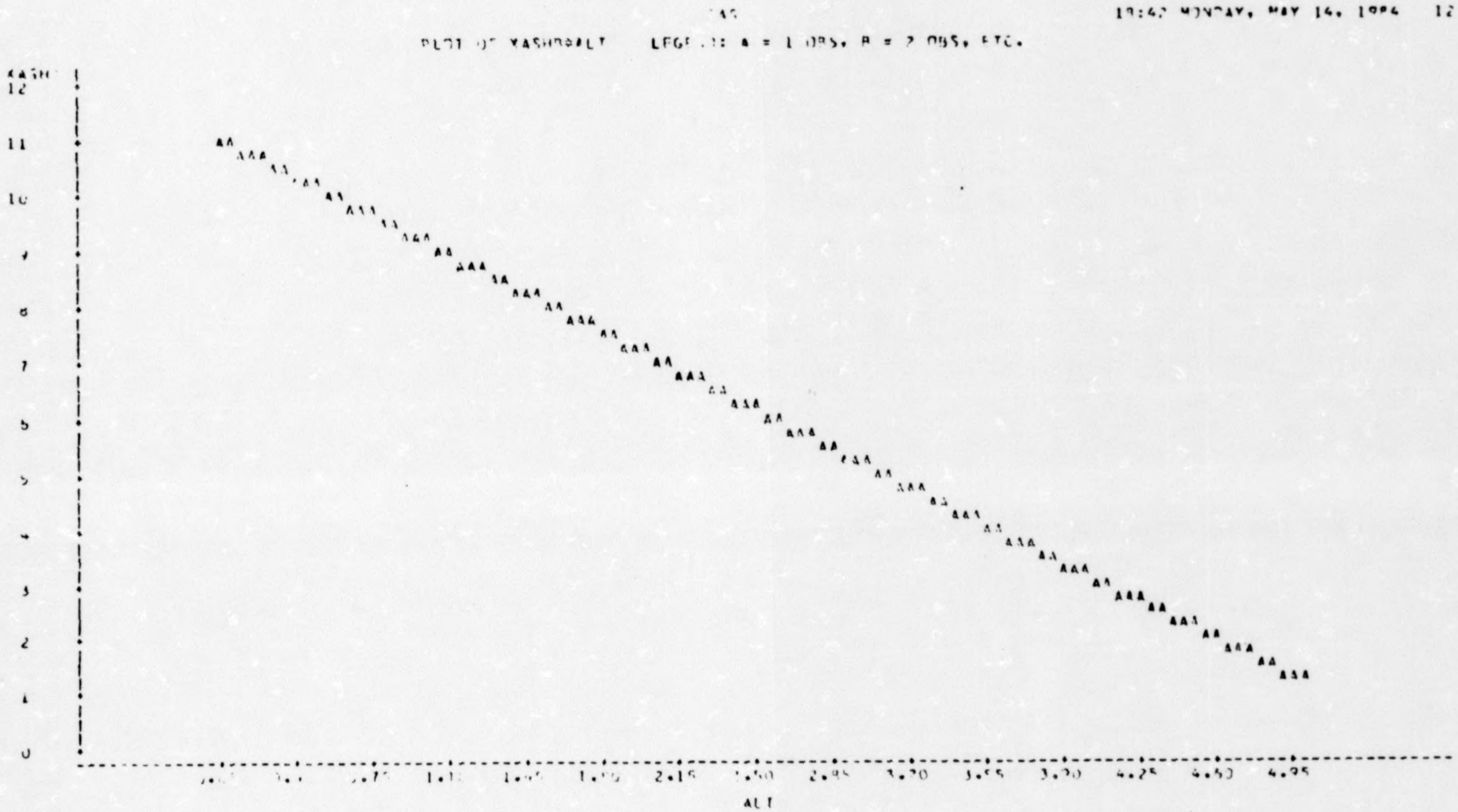


Figure 23. Percent ash in the residual versus percent added nitrogen at 425°C.

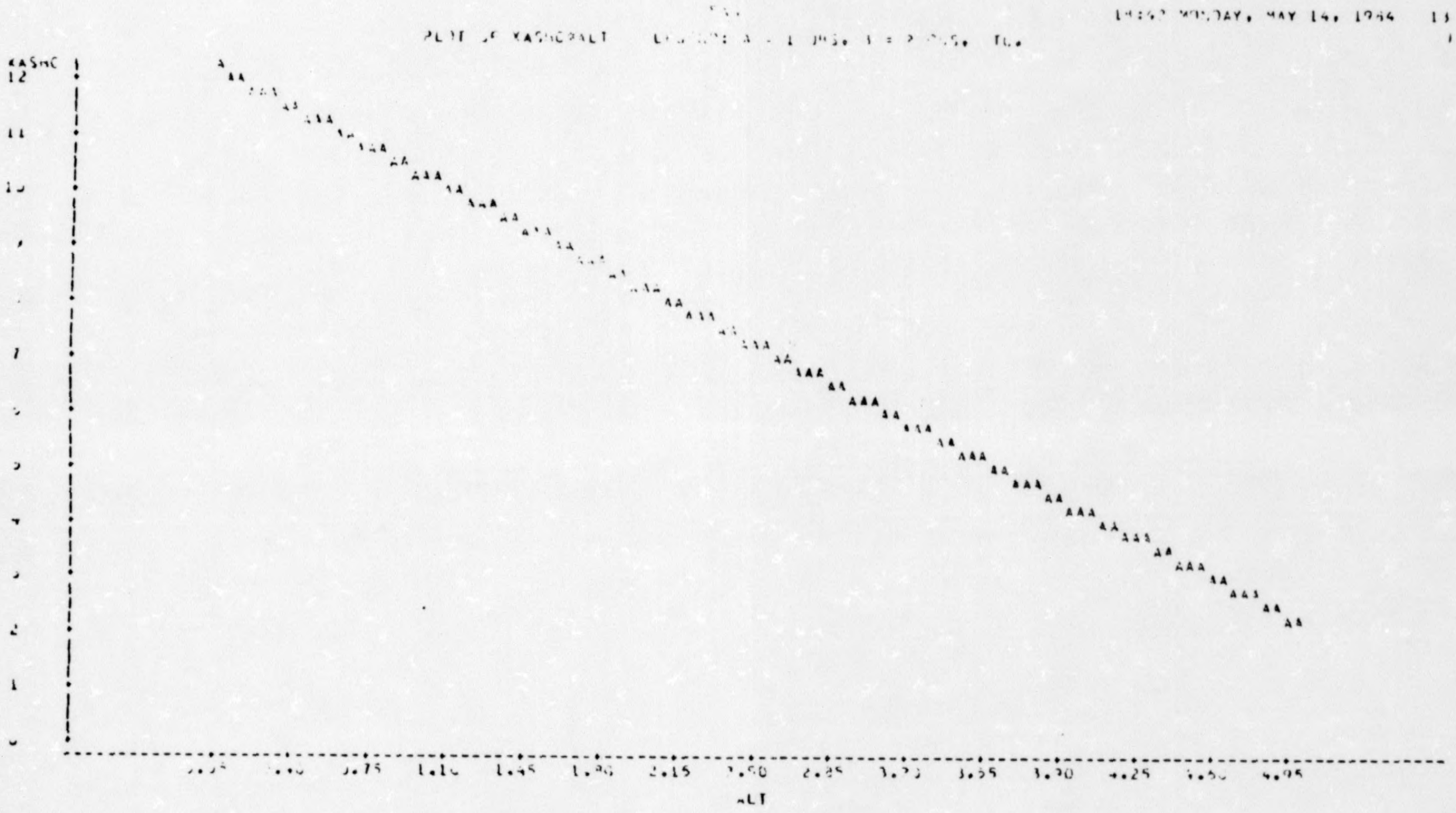


Figure 24. Percent ash in the residual versus percent added nitrogen at 600°C.

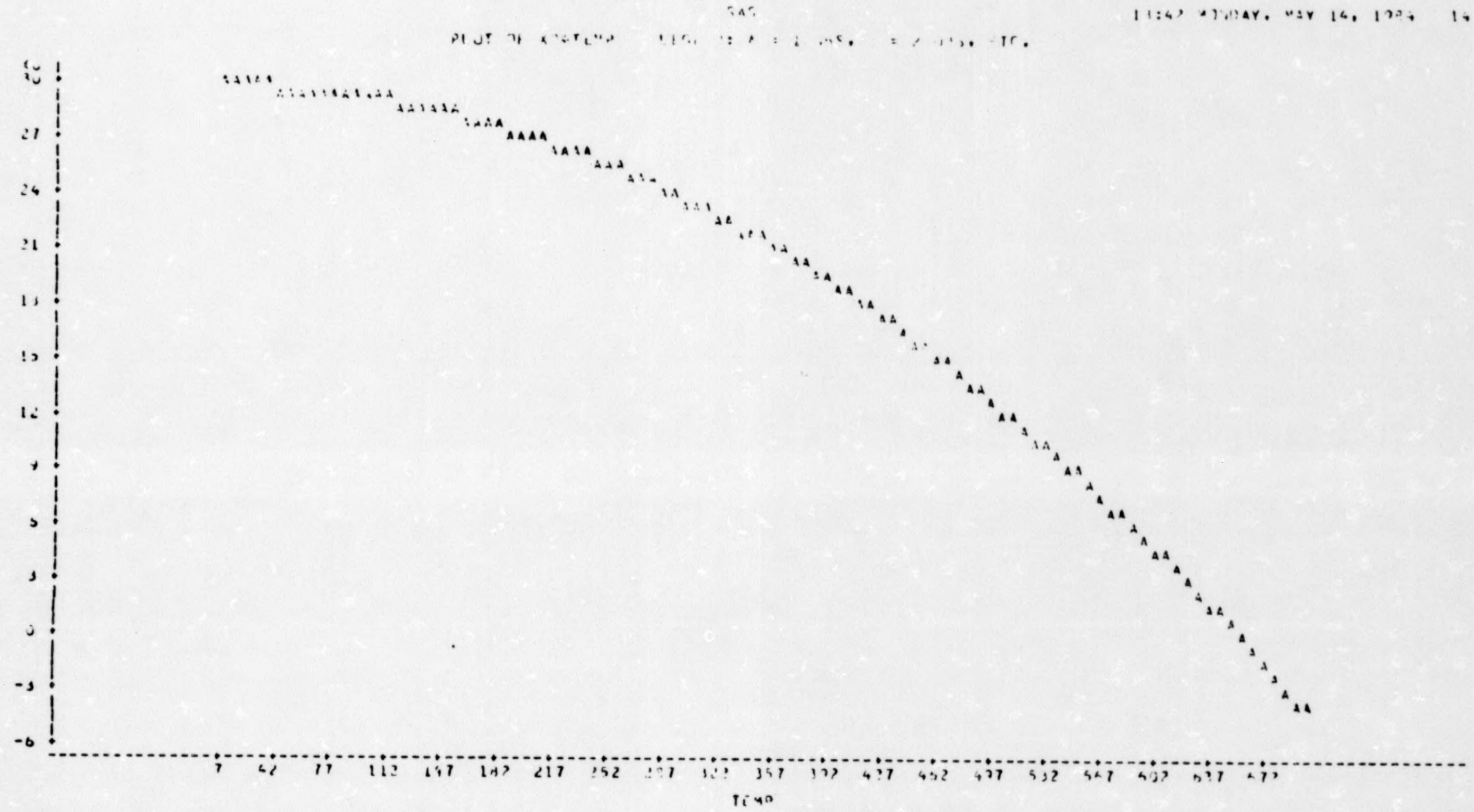


Figure 25. Percent oxygen in the residual versus temperature.

CHAPTER V

DISCUSSION

Table 4 is a list of the parameters investigated in this research and the levels at which each parameter was studied. Because of the nature of this research, the degree of nitration, or percent added nitrogen, was the process variable of most interest to the investigators. The levels used were not chosen specifically, but the treatment of the lignite splits discussed in Chapter III dictated two of the levels. The third level (untreated lignite) was included in the study because of the need for a "blank" and a desire to have a basis of comparison with other assays.

The percent added nitrogen, the measure of the degree of nitration, was determined using the ultimate analyses of the coals (Table 6) and Equation 18. The percent carbon is used as a measure of how much organic material is present in the coal. The C'/C ratio is a way of normalizing the new nitrogen content. This assumes that nothing extracted during the nitration procedure substantially affects the ultimate analysis of the coal.

The other four parameters (soak temperature, soak time, pressure, and sample mass) were investigated in this study in order to have some additional means of comparison to other assays in the literature. The soak time and pressure levels were chosen for convenience. Helium was used as the inert gas so that N_2 generated during pyrolysis could be detected.

The sample mass levels were restricted by the size of the bomb and the expense of treating coal with purchased nitronium salts. The temperature level of 600°C was chosen as a temperature typical of low-temperature carbonizations; the temperature level of 250°C was chosen on the basis of earlier thermogravimetric studies of a nitrated HVC bituminous coal which indicated that it rapidly devolatilized at this temperature.(3) The temperature level of 425°C was chosen as a midpoint between 250 and 600°C.

The purpose of an experimental design like that used in this research, coupled ith regression analysis of the data, is to save time. When the analysis of the data is complete, a series of predictive equations, along with key statistical data, is generated. These equations allow one to predict the value of a dependent parameter on the basis of a given set of independent parameters. For example, Equation 19 in Table 10 allows a prediction of the total gas yield for a pyrolysis reaction at a given temperature.

A predictive equation tells certain things about the effects of the studied independent variables on the dependent variable. Equation 19 in essence tells us the volatile yield is dependent solely on the temperature of pyrolysis. Because the coefficient of the temperature is positive, the equation tells us that an increase in the temperature of pyrolysis will give an increase in the total gas yield.

It is important to keep in mind that a regression is applicable only to the range of parameters studied in the investigation. For example, predicted effects of temperature on the volatiles yield are valid only over the 230 to 600°C range. Also, because regression equations have no limiting values, nonsensical values of less than 0 and greater than 100 percent can sometimes be found in graphs of a predictive equation.

A statistical term is used repeatedly throughout this study, "correlation coefficient." A correlation coefficient is the square root of the sum of the squared differences between the actual and predicted value plus the predicted value. The correlation coefficient is a measure of the efficiency of a model, that is, whether its predictions are real or due to chance. A correlation coefficient of either +1 or -1 indicates that the effects are real and that no random error exists, while a correlation coefficient of 0 indicates that the data points are simple random.(33)

In Table 10, many of the equations contain square terms, such as $(\text{Temperature})^2$, and so forth. Because few things in chemistry are perfectly linearly related, a square term will often give the regression equation slightly more accuracy.(32)

In the remaining discussion, all values given are on a moisture-free basis. In the discussion of the predictive equations, the calculated yields from a given equation will be mentioned as approximations. Because none of the predictive equations have a correlation coefficients variance of 1, they do not predict a given effect with 100% accuracy.

Table 7 contains a list of the yields of volatiles yields for the 34 3xperiments run in this research. The percentage of volatile materials here is essentially the yield of gaseous materials. When the coal was pyrolyzed, most of the water generated stayed with the solid phase, as did most of the organics. Since the determination of percent volatile yield was done by difference, the small droplets of water and the thin film of organics that would accumulate under severe pyrolysis conditions would provide a small source of error. However, the regression equation for the total gas yield in Table 10 has a correlation coefficient of 0.95. Thus, the model equation is valid, and gives an accurate representation of the dependence of the total gas yield upon the investigated parameters.

For this reaction system, the total gas yield is independent of sample mass, initial helium pressure, residence time of the solid, and level of nitration. The first is expected, since the gas yield is a percentage value of the sample weight. With a larger sample, larger amounts of gas will be evolved, but the percentage of the sample mass should be the same as for that of smaller samples.

The lack of dependence of the volatiles yield on pressure is contradictory to the study by Sustmann and Siesecke. However, their experiments may predict a non-existent effect. From their data for the Saxon lignite pyrolysis, they noted only a 15% increase of total gas yield for 1 to 50 atmospheres pressure (27.8 to 32.1%).(24) By the same token, the lack of dependence on pressure could be due to the experimental errors in this report.

The lack of dependence of the yield of volatiles on residence time may be an artificial effect due to the length of the shortest residence time used (0.5 hrs). Thus, 0.5, 1.5 and 2.5 hours may all be "long" residence times, thereby agreeing with Table 2.

The effect of nitration on the volatiles yield of lignite pyrolysis was not what was expected. Thermogravimetric studies of a nitrated high-volatile C bituminous coal by Sohio researchers showed that at 250°C under N_2, the coal underwent a 90% weight loss almost immediately. Bituminous coals are less substituted and more aromatic in character than are lignites. Therefore, more sites are available for nitration, and the increased aromaticity will cause the bituminous coals to simulate explosive trinitrobenzene derivatives more readily. Also, lignites have a higher content of volatilizable material (small molecules, $-CO_2H$, and -OH groups) than an HVC coal; so the effect of nitration would not be so noticeable on lignite as it would on the higher-ranked coal.

The dependence of the volatiles yield on temperature is obvious from Figure 9 and Equation 19. Such dependency is in harmony with the studies reviewed in Chapter II. As temperature goes up, volatile materials are driven off; when the pyrolysis temperature gets high enough, the tars and even the matrix decompose to form gases. AT 250°C, the volatiles yield should be close to 4.5%, much less than the 90% weight loss for a nitrated HVC bituminous coal. If the treated and untreated lignites were pyrolyzed at 550°C (fischer assay temperature), the yields of gas should be approximately 28.2%, which is somewhat greater than yields of gas reported in the literature.

The effects of varying temperature, pressure, time, sample weight, and level of nitration are not noticeable when examining the oils yield. This independence could be due to experimental errors, it could be due to the long cool-down period which would allow the tar to polymerize, and it could be due to the way in which the oil yield was determined. The oil yield was determined by weight difference and not by evaporating the hexane and weighing the extract. The initial weight was taken to be the weight of the pyrolysis residue. The final weight was taken to be the weight after vacuum-drying the extraction thimble containing the coal. If any of the hexane stayed with the coal, it would cause error in the oils yield determination. One would expect nitration to increase tar yield if the nitrating procedure kept oxidation at a minimum. Unfortunately, this is not the case.

No definitive statements can be made about the yields of asphaltenes are preasphaltenes, since the solvents used tended to swell the coal and become irrevocably integrated with the coal. Washing with methanol after extraction to displace the toluene or THF with a more easily removable molecule might allow more accurate determinations of the yields of these quantities.

The residual yield is the weight of the coal after it has been extracted with hexane, toluene, and THF. Herein is a source of error, as the weight of adsorbed solvents will change the weight of the coal residual artificially. However, this fact does not seem to be of major importance, since the predictive equation for the residual yield (Equation 20 in Table 10) has a correlation coefficient of 0.95, indicating a high degree of accuracy in predicting the effects of the parameters investigated in this research.

The comments on the effects of sample mass on the yield of gas are applicable here as well. Pressure and soak time in a closed system might be expected to increase char yields due to tar polymerization. But long residence times also cause char yields to be diminished, since the coal has more time to decompose. Nitration, for reasons mentioned in the discussion on the volatiles yield, would be expected to decrease the output of char. In reality, the yield of char is independent of all these factors for this reaction system.

Temperature increases would be expected to decrease char yields because as more and more energy is pumped into the reactor the more the coal will decompose. Figure 10 shows that this is exactly what happens. At 250°C, the residual yield would be expected to be close to 92%, as opposed to 10% for the aforementioned HVC bituminous coal. At Fischer assay temperature (550°C), one would expect to see a char yield of 69%, a value comparable to values found in literature assays.

The percent carbon in the residual follows trends similar to those uncovered by other researchers.(20,21) Equation 21 in Table 10 is the predictive equation generated by the regression analysis. Equation 21 has a correlation coefficient of 0.96, again indicating a strong degree of reliability.

One more, sample mass, pressure, soak time and nitration have negligible or unapparent effects on the percent carbon in the residual. The sample weight would of course have no effect on the percentage of any element (unless the heat-transfer effect was sufficiently great) for the same reason it would have no effect on the percent volatiles yield. Long soak times might be expected to increase carbon content in the residual since, as the coal is heated for longer times, more volatile elements (like hydrogen and oxygen) would be expected to be removed. The lack of dependence of the percent carbon in the residual is undoubtedly due to the time range which was employed, as was the long cool-down time. Probably only very long residence times would affect the content of carbon in any noticeable way, due to increasing ring condensation. Nitration independence of the residual carbon content is inexplicable.

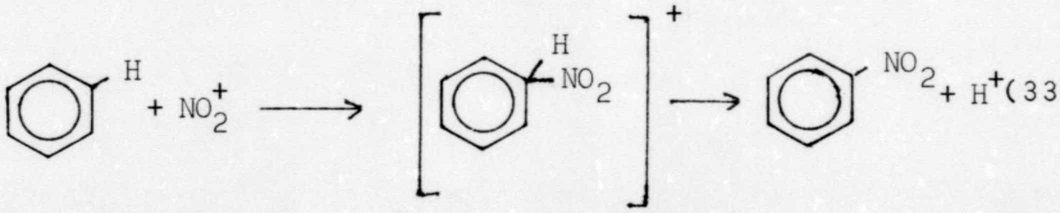
The temperature dependence of the residual carbon content is explained by the removal of other more volatile elements at higher temperatures, and the corresponding coking of the char. The effect of temperature increases on the residual carbon content is graphically depicted in

Figure 11. At 550°C, the char carbon content for these experiments should be close to 75%, a value comparable to literature values.(12,20) The prime source of error is the presence of adsorbed toluene and THF as mentioned earlier.

The predictive equation for the hydrogen content is less dependable than other predictive equations in Table 10. The equation has a correlation coefficient of 0.90. The equation is still a good predictor of the dependence of hydrogen on the independent parameters listed in Table 4.

The char hydrogen content is independent of sample mass for reasons similar to those mentioned in the discussion of the volatile yield dependencies. The lack of time dependency is, in all likelihood, due to reasons similar to those mentioned in the discussion of the residual carbon content. The lack of pressure dependency of the char hydrogen content is presently inexplicable. One might have expected a greater char hydrogen content at higher pressures, since hydrogen containing species (water, aliphatic compounds) volatilize readily. Yet such is not the case.

The hydrogen content is dependent of the level of nitration. During the nitration process, hydrogen in an aromatic system is lost, as shown in Equation 33.



(33)

This hydrogen removal shows up in the pyrolysis char.

The hydrogen content of the char is most dependent, according to the regression analysis, on the temperature. Increasing temperature removes water, both adsorbed and that from the coal decomposition; increasing the pyrolysis temperature also removes saturated hydrocarbons from the coal, thus decreasing the H/C ratio in the char. At 550°C, for an untreated lignite, the char should contain approximately 3.6% hydrogen; a lignite with 3.56% added nitrogen at the same temperature should have a residual with close to 3.0% hydrogen. Both these values are similar to literature values, although the nitrated coals have substantially less hydrogen than the untreated coal.

The effects of increasing the nitration levels and temperature on the char hydrogen content are depicted in Figures 12, 13, 14 and 15. Figures 13, 14 and 15 are two-dimentional analogs of Figure 12. One can look at the contour plot and see th-t, for a given temperature, as the nitration increases, the residual hydrogen content decreases; from the same graph it can be seen that, for a given level of nitration, an increase in temperature reduces the char hydrogen content. Figures 13, 14 and 15 show the same effects of changing the nitration level for a given pyrolysis temperature.

The predictive equation for the char nitrogen content is a good predictor of the nitrogen content in the residual. Equation 23 in Table 10 has a correlation coefficient of 0.96. Only the level of nitration has any noticeable effect on the nitrogen content of the char.

The lack of dependence of the percent nitrogen in the residual on sample mass is, of course, due to the same reason that the char carbon and hydrogen contents are independent of the sample weight. Because nitrogen which occurs naturally in coal is not a readily volatilizable element, pressure, which affects only volatile materials directly, has no effect on the residual nitrogen content. Nitrogen is found primarily in the form of cyclic amines in coal. These compounds are not easily decomposed; thus, time and temperature have no visible effects over the ranges examined in this investigation. At higher temperatures, especially those above 700°C, and for longer soak times, nitrogen would volatilize and then the char nitrogen content would decrease. When nitrogen does volatilize, it comes off as NH_3 organic amines; NO_x gases are almost never seen, due most probably to the low amount of nitro groups in non-pretreated coals.

When coal is pyrolyzed at low-temperature carbonization conditions, very little nitrogen is removed.(12,20) Because nitrated lignite does not exhibit the explosive character of a nitrated bituminous coal, but rather has traits like those of an unaltered coal, essentially no nitrogen is removed during low-temperature carbonizations. At a nitration level of 3.44% added nitrogen, the char should contain above 4.12% nitrogen. If the lignite had undergone rapid devolatilization, most of the nitrogen should have been removed.

The effects of increasing nitration level of a coal can be seen in Figure 16, where the char nitrogen content goes from 1.28% to 4.28% at nitration levels of 0.05% to 4.05%, respectively. High nitrogen content in the char reduces its usability as a fuel or substrate for still further synthetic fuel processes. Burning a high nitrogen char will give off unacceptably high NO_x levels, and using such a char for further processing will lead to the same thing unless nitrogen compounds are removed. Catalysts for upgrading are poisoned by nitrogen compounds in coal and coal liquids, because they complex with the metals in the catalyst, preventing further upgrading reactions.(27)

Errors in this evaluation would stem from normal experimental errors and from the adsorbed solvent problem mentioned earlier. Here, however, the adsorbed solvent problem is minimized, as neither toluene nor THF contain nitrogen.

The sulfur content of the residual char is predicted adequately by Equation 24 in Table 10. Equation 24 has a correlation coefficient of 0.94. Errors in this equation would stem from normal experimental error and from the adsorbed solvent problem. Again, the absence of sulfur in toluene and tetrahydrofuran reduces the latter problem. Figure 17 is a contour plot of Equation 24; Figures 18, 19 and 20 are plots of the char sulfur content versus temperature at constant nitration levels of 0, 2.39 and 3.44% added nitrogen, respectively.

Sulfur content is not dependent on the sample mass for the same reason the carbon, hydrogen and nitrogen contents are not. Because sulfur is not easily volatilized, pressure changes should not affect the char sulfur content. The residence times studied are apparently insufficiently long to alter the residual sulfur percentage.

Nitration decreases sulfur content at a given temperature due to the fact that sulfur is removed during the pretreatment.(2,34) The reduction is substantial, as can be seen from Table 6. Higher temperatures increase the sulfur content in the residual due to the removal of other more easily volatilized elements, like hydrogen and oxygen. Often, during pyrolysis sulfur is evolved as H_2S, but the amount is small enough to go unnoticed; incidentally, no H_2S was detected in teh GC analysis of the pyrolysis gases.

The dependency of the sulfur content of the char on both nitration and temperature are obvious in Figure 17, where, for a given temperature, the char sulfur content decreases in coals with higher percentages of added nitrogen. Figures 18, 19 and 20 break down the three-dimentional Figure 17 into two dimentions and show the same thing as the contour plot. Each of the three two-dimentional plots show a sulfur percentage increase as the pyrolysis temperature is raised and, from graph to graph, for a given temperature, the more extensive the nitration, the less the sulfur content. Here is a very positive benefit of nitration.

Fischer assay conditions (550°C) for an untreated lignite should give a char sulfur content of 1.02% is comparable to literature assays.(12,20) A coal with 3.44% added nitrogen should yield a Fischer assay char with 0.45% sulfur; this value is comparable to literature values for coals with reduced sulfur content.(12)

The predictive equation for the ash content of the char is Equation 25 in Table 10. This equation has a correlation coefficient of 0.94. Again, this equation is a good model for determining the effects of time, temperature, sample mass, pressure, and level of nitration on the residual ash content. Figure 21 is a contour plot of Equation 25, and Figures 22, 23 and 24 simplify this complex equation by plotting ash content in the cahr against the level of nitration. Possible errors in the evaluation of the char ash content dependencies are similar to those for the char sulfur determination.

The lack of dependency of the ash content on the sample weight is again for reasons identical to those mentioned in the discussion of the char carbon content. Because, under low-temperature pyrolysis conditions, the ash constituents of lignite are essentially non-volatile, pressure and soak time have no real effects. Temperature increases increase the ash content artificially by removing the organic components of the coal, as well as moisture. For this reason, very long residence times might also play a small role in increasing the residual ash percentage, but not, apparently, over the range of times examined in this study.

The ash content of the char is most influenced by the level of added nitrogen. Ash is removed during the treatment process. Table 6 shows that nitrated coals have lower ash contents than untreated coals. The removal of ash during the pretreatment could be physical or chemical.

The nitration process appears to swell the coal due not only to the presence of the NO_2^+ ion but also the solvent nitromethane. It is possible that, during the swelling, some ash particles are removed. The NO_2^+ ion is an excellent oxidant; the oxidation of pyrite and marcasite by this cation, and the subsequent removal thereof, may also account for the low ash content of nitrated coals. One other effect is that of the physical addition of nitro groups to a coal, which will reduce the percentage of ash just from the increase in the percentages of nitrogen and oxygen. Thus, another benefit of nitration, that of de-ashing, is readily seen.

At 550°C, according to Equation 25 in Table 10, one would expect the ash content of an untreated lignite to be approximately 12%; for a coal with 3.56% added nitrogen, the char ash content should be 4.9%. The former is comparable to literature values, but the latter is drastically reduced.(12,20)

The determination of oxygen in coal has always been a controversial problem, since no good, readily available assay for oxygen exists. Computing oxygen content by difference is fraught with error, for this method does not take into account oxygen in the mineral matter, the presence of other elements (for example, chlorine) not considered a part of the ultimate analysis. These errors are present in all coal studies where oxygen determination is carried out by difference. When the same error is consistently made, the error is negated. Thus, the values for the char oxygen content should be comparable to other studies.

The prime source of error in the investigation of char oxygen content is the adsorbed solvent problem discussed earlier. In this case, the oxygen atom in tetrahydrofuran makes the problem more acute.

The predictive equation is Equation 26 in Table 10. Equation 26 has a correlation coefficient of 0.96. The value gives Equation 26 a high degree of accuracy. Such accuracy indicates the THF problem was a problem not so severe as expected.

The lack of dependence of the char oxygen content on sample is explained in the same manner as the independence of the carbon, hydrogen, sulfur and ash analyses of the char. One might expect pressure increases to increase the oxygen content of the char, but it does not. Perhaps the effect of pressure is masked by that of temperature, or such an effect may simply be non-existent. Long soak times would deoxygenate coal, but undoubtedly the minimum soak time of 0.5 hours is long enough that longer soak times will have no appreciable effect in deoxygenating coal.

The lack of dependence of the char oxygen content on the level of nitration is curious but understandable. Nitration increases the oxygen content of coal both through oxidation and through the addition of two oxygen atoms per nitro group added to the coal. These effects can be seen from Table 6, which contains the elemental analyses of the base coals used in this research. The oxygen content of lignite is so high that oxidation is minimal and the nitro group oxygens do not drastically change the coal oxygen content. Under thermal decomposition conditions, the oxygen atoms will readily combine with available hydrogen atoms to form water, or with activated carbon to form carbon oxides. Thus nitrating the lignite should not appreciably affect the residual oxygen content.

The effect of increasing the pyrolysis temperature on the char oxygen content is observed in other published studies. Oxygen in the char is decreased by raising the temperature of pyrolysis, thereby volatilizing more and more oxygen. Figure 25 shows this clearly. At 550°C, the oxygen content of the lignite chars should be about 8.4%, which is comparable to literature studies. Such studies show lignite chars to contain 9 to 10% oxygen (moisture-free basis).(12,20)

The analysis of the pyrolysis off-gases by gas chromatography was described in Chapter III. The gases observed on the gas chromatograph were H_2, N_2, O_2, CO, CH_4 and CO_2 in that order of retention time. Because air sometimes leaked into either the pyrolysis reactor (during cool-down), the gas-sample bomb, or the GC itself, all oxygen in the chromatogram was assumed to come from the air. Molecular nitrogen determination was calculated by determining the amount of O_2 present, multiplying the value by the N_2/O_2 ratio of air, and subtracting this amount of molecular nitrogen determined by the GC. The remainder was assumed to be the amount of nitrogen generated by the coal during pyrolysis.

The analysis of the off-gases from the pyrolysis runs had several places for error. The Parr bomb tended to leak from time to time. The sample bombs leaked while samples were removed with a syringe. The detector on the GC was not very sensitive to H_2, especially in low amounts. The limited number of observations of the actual presence of the gases may have introduced errors into the regression analysis. Also, the wrong mathematical functions of the independent parameters may have been used in the regression. However, to avoid excess complexity, the researchers decided to keep in independent parameters in as simple a form as possible, for ease of understanding. One can introduce falsehoods into a model equation by using an overly complex function, and then will not be able to interpret the data, either.

The consequence of these facts is that the content of the off-gases appear to be essentially unpredictable, at least on the basis of the regression analysis used in this research. This holds especially true for H_2, N_2 and CO. The methane and carbon dioxide contents in the off-gases are only barely predictable. Therefore, either the off-gases are truly independent of the parameters listed in Table 6, or else the wrong functions were used in the regression analysis were used. It could mean also that the experimental errors overshadow the effects of the independent parameters.

That the off-gas contents are totally independent of the parameters listed in Table 6 is unlikely. Literature studies have been done to show that things like pressure and temperatuer do in fact change the gas contents. Some of these reports are reviewed in Chapter II. Sample mass should have little effect on the off-gas contents, but soak time should change the contents, as more time is allowed for gas-phase and gas-solid reactions which do change the off-gas makeup. Nitration should cause a pyrolyzed coal to yield more N_2, NH_3 and NO_x gases than untreated coals. Temperature and pressure effects on the pyrolysis gas make-up are discussed in Chapter II. Unfortunately, this research shows very little of these effects. Because the off-gas predictive equations are so questionable (as shown by their relatively low correlation coefficients), no effort to explain these results was made in this paper.

One other gas was evolved during this research, ammonia. The generation of ammonia during coal pyrolysis is not unknown.(14,15) Ammonia was detected not by gas chromatography, but by smell and the presence of crystals of NH_4HCO_3 on the inside of the bomb after certain pyrolysis reactions (see Table 9). The identity of these crystals was established by infrared and X-ray analysis. NH_4HCO_3 crystals are generated from ammonia, water and carbon dioxide, as shown in Equation 34.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3 \qquad (34)$$

During the experiments where these crystals were noted, CO_2 had been evolved in large amounts (see Table 9) and the smell of ammonia was noticed upon opening the bomb. Only in experiments where nitrated lignite was the pyrolyzed coal was ammonia given off, indicating that nitrated coals give enhanced yields of NH_3 as opposed to unnitrated coals. The increased nitrogen content of the nitrated coals is unquestionably the source of the enhanced ammonia yields.

CHAPTER VI

SUMMARY

In this research, the primary goal was to determine how the pyrolysis of nitrated lignites differed from the pyrolysis of an untreated lignite under low-temperature carbonization conditions. The secondary goal was to evaluate the effects of sample mass, pressure, temperature and residence time on the pyrolysis of both untreated and nitrated lignites. Specifically, the yields of char, gas, oils, asphaltenes, and preasphaltenes were measured; in addition, the ultimate analysis of the pyrolysis chars was studied, as well as the content of the off-gas.

Pyrolysis is an old and well-studied process, especially low-temperature pyrolysis. The effects of numerous parameters on pyrolysis yields have been investigated. The chemistry and kinetics of pyrolysis are well understood.

Treating coal with nitrating agents is not new, but using nitration as a beneficiation process for pyrolysis is a novel concept. Unfortunately, nitration appears to benefit low-temperature lignite pyrolysis very little. It does not increase the volatiles yield of lignite or decrease the yield of char. Nitration increases the nitrogen content and decreases the hydrogen content of the coal, and pyrolysis removes almost none of the added nitrogen.

Nitration does desulfurize and de-ash the coal, and seems to increase the yield of ammonia. Nitration apparently does not significantly change the content of the pyrolysis off-gas, nor does it have any apparent effect on the char carbon and oxygen contents.

The effects of varying sample mass, pressure, temperature, and residence time are those expected from previously published investigations. Temperature is, naturally, the dominant factor in affecting the pyrolysis products.

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