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Assay Carbonation of Lignite from the Northern Great Plains Province

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Equations recommended for predicting carbonization yields of Northern Great Plains Province lignites, on an m.a.f. weight percent basis are:

$$\text{Char yield} = 94.4 - 0.0951(T, {}^\circ C) + 0.000050\ (T, {}^\circ C)^2 + 0.530\ (F.C.) - 4.31\ (H_2)$$

$$\text{Tar plus light oil yield} = 26.9 - 0.0320\ (T, {}^\circ C) + 0.000019\ (T, {}^\circ C)^2 + 0.000688\ (Btu - 11{,}700) - 0.0389\ (C/H_2)^2$$

$$\text{Product gas yield} = 1.59 + 0.0393\ (T, {}^\circ C) - 0.000012\ (T, {}^\circ C)^2 - 0.383\ (F.C.) + 0.956\ (O_2)$$

At 500° C, these equations reproduced experimental data more precisely than did equations developed by other investigators, exclusively for this temperature.

Since weight of charge was significant at the 95 percent or higher confidence interval for seven of nine yield factors, a constant weight of charge should be specified for future assay carbonization work.

This abstract of a thesis, submitted by Daniel C. Boteler in partial fulfillment of the requirements for the Degree of Master of Science in the University of North Dakota, is hereby approved by the Committee under whom the work has been done.

Wayne R Kube
Chairman

Jean R. Jensen
A W Cooley
James L. Elder

Christopher J. Hamre
Dean of the Graduate School

ASSAY CARBONIZATION OF LIGNITE FROM THE NORTHERN GREAT PLAINS PROVINCE

By

Daniel C. Rotzler

B.S. in Chemical Engineering, University of North Dakota, 1964

A Thesis
Submitted to the Faculty
of the
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for the Degree of
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ABSTRACT

The purpose of this investigation was the determination of the significance of temperature, source (mines), moisture content, and weight of charge on various carbonization yield factors, using a Greco-Latin square experimental design with replication. Empirical equations for predicting product yield factors were to be developed as functions of temperature and lignite composition. Five Northern Great Plains Province lignites were carbonized at five temperature levels between 500° and 1,000° C, at five moisture contents, and using five weights of charge.

An analysis of variance indicated significance of mines, carbonization temperature, and weight of charge at the 99 percent confidence interval for yields of char, tar plus light oil, and product gas. Neither moisture content nor replication were significant at the 95 percent confidence interval.

Multiple regression equations for predicting seven different factors of carbonization yields were developed using an IBM 1620 computer. Equations recommended for predicting carbonization yields of Northern Great Plains Province lignites, on an m.a.f. weight percent basis are:

$$\text{Char yield} = 94.4 - 0.0951\ (T,\ ^\circ C) + 0.000050\ (T,\ ^\circ C)^2$$

$$+ 0.530\ (F.C.) - 4.31\ (H_2)$$

$$\text{Tar plus light oil yield} = 26.9 - 0.0320\,(T, ^\circ C) + 0.000019\,(T, ^\circ C)^2 + 0.000688\,(\text{Btu} - 11{,}700) - 0.0389\,(C/H_2)^2$$

$$\text{Product gas yield} = 1.59 + 0.0393\,(T, ^\circ C) - 0.000012\,(T, ^\circ C)^2 - 0.383\,(\text{F.C.}) + 0.956\,(O_2)$$

At 500° C, these equations reproduced experimental data more precisely than did equations developed by other investigators, exclusively for this temperature.

Since weight of charge was significant at the 95 percent or higher confidence interval for seven of nine yield factors, a constant weight of charge should be specified for future assay carbonization work.

INTRODUCTION

The major purpose of this investigation was to determine assay carbonization yields of lignites from the Northern Great Plains Province as functions of temperature of carbonization, source (mine), moisture content, and weight of charge. Yield factors of interest include: char, tar and light oils, hydrogen sulfide (H_2S), quantity and heating value of product gases. Empirical prediction equations were to be developed for each yield factor as the dependent variable, with carbonization temperature and one or more factors of the proximate and/or ultimate analyses of the coals as independent variables.

Carbonization of lignite is of interest because of possible uses of chars for blending with coking coals in the production of coke for blast furnace operations, for reduction of taconite or other iron ores, or as an upgraded smokeless fuel for domestic use and/or power generation plants. Tars and light oils are potential sources of liquid fuels, benzene, naphthalene, toluene, and xylene, while heavier molecular weight components could be used as a crude fuel oil, or refined into lighter fractions. Carbonization gases, especially if enriched, could be used for commercial and industrial heating under the proper economic circumstances.

Specifically, the scope of this work was to carbonize lignite from five mines in a bench-scale unit at temperature levels from 500° to 1,000° C. The influence of moisture content of the charge from 15 to 35 percent and the mass of the charge from 120 to 160 grams were also to be investigated. The series of tests were arranged in a Greco-Latin square design of four variables at five levels each, requiring 25 tests to complete the square. Since the tests were to be made in duplicate, a total of 50 were required.

It was expected that the temperature level and source of lignite would be significant, but that moisture content and mass of charge would not. In previous work it had been assumed that moisture content and mass of charge had no significant influence on yield parameters, but this assumption had not been verified.

A literature survey was made, particularly of past Bureau of Mines publications, to determine the work reported to date on bench-scale carbonization of coal, and past success at developing product-yield prediction equations for other coals.

CHAPTER I

BACKGROUND AND HISTORY OF ASSAY CARBONIZATION

Carbonization of coal in the United States began in beehive coke ovens, where the resultant coke, or char, was the only desired product. Later on, by-product coke ovens were developed, in particular the slot-oven, designed for operating temperatures of 800° to 1,100° C, with extensive auxiliary equipment for collecting by-products such as tars, crude light oils, product gases, ammonium sulfate, naphthalene, and others. The slot-ovens have gradually replaced the beehive ovens for coke-making over the years. In 1946, of the 79 million tons of coke produced in the United States, over 71 million tons were produced in slot-ovens (20).[1/]

Low-temperature carbonization, generally accomplished at temperatures under 700° C in metal retorts, has been popular in Europe because it produces a comparatively smokeless fuel, is easily ignited, and is well suited for domestic use in homes that lack central heating. Tar yields are greater, but contain less aromatic compounds. Ammonia and gas yields are lower, but the gas usually has a higher heating value. To date, the United States market for low-temperature carbonization products is almost exclusively confined to the manufacture of briquets for outdoor cooking (21).

[1/] Numbers in parenthesis refer to items in List of References.

Bench-Scale Carbonization Methods

Fischer-Schrader method

Due to the growing interest in the carbonization properties of American coals, a joint cooperative survey was begun in 1928 by the U.S. Bureau of Mines and the American Gas Association. The Fischer-Schrader assay carbonization method, as reported in 1920, was selected from among three bench-scale methods considered (31). This method utilizes an aluminum retort, externally gas-heated with a Meker burner, to carbonize approximately 50 grams of -20 mesh coal at 500° C (32).

USBM assay carbonizer

After considerable experience with the Fischer-Schrader method at the Denver Station of the U.S. Bureau of Mines, it was decided to devise an assay carbonization unit that was inherently more accurate. The Fischer-Schrader unit was not gas tight, did not remove hydrogen sulfide from the gas stream, and made no direct measurement of the volume of gas produced. In 1950 the "precision laboratory carbonization-assay apparatus," hereafter referred to as the "USBM assay carbonizer," was developed. Mass balances of 100 ±0.5 percent are readily obtainable with this latter unit. Although the unit was initially developed for operation at 500° C, a modified furnace and retort assembly were later designed for use at temperatures to 1,000° C, which is essentially the average operating temperature employed in commercial high-temperature carbonizers. These units are nearly the same as those used in the present investigation.

The U.S. Bureau of Mines-American Gas Association laboratory-size coal carbonizer (BM-AGA), designed for a charge of 100 to 200 pounds, gives approximately the same weight ratio of product yields as a 500 pound capacity experimental slot-oven type carbonizer (7). Variations in types of industrial carbonization equipment and in operating conditions limit the correlations between pilot plant and industrial data. However, results indicate that a high degree of correlation between BM-AGA and industrial yields can be obtained, if operating variables are held relatively constant (37).

Comparison with BM-AGA carbonization

A considerable number of experimental tests have been made on bituminous and subbituminous coals, in an attempt to correlate carbonization yields from the BM-AGA retort-type unit with the Fischer-Schrader assay carbonization method. Correlation results indicated that BM-AGA yields of coke, tar, light oil, gas, and liquor can be calculated from data obtained from the Fischer-Schrader assay method, using the prediction equations developed from comparative yield ratios. Accurate assay results can indicate comparative product yields from different coals in commercial units that approximate the BM-AGA method quite closely (38).

Although a considerable amount of work has been done over the past 40 years by the Bureau of Mines on bench-scale type carbonization of coal in externally heated retorts, only limited attention has been given to lignites. Most of the test data on lignites has been obtained at 500° C. A series of lignites from North Dakota and of selected coal bed components (anthraxylon, fusain, opaque and translucent attritus), have both been carbonized at 500° and 550° C in a duplicate of the USBM assay carbonization unit. The results indicated that, with few exceptions, there was little evidence of geographic effect on product yields of low-temperature carbonization. The following data indicates the range of product yields obtained, expressed as weight-percent of moisture- and ash-free (m.a.f.) charges for fuel-grade lignites (18):

Char	64.2 - 74.4
Water of formation	8.9 - 12.2
Tar, dry	3.3 - 8.9
Light oil	0.9 - 2.2
Product gas; O_2-N_2 free	10.0 - 15.9
Hydrogen sulfide	0.1 - 1.5

Prediction Equations

Regression equations with multiple correlation coefficients have been developed for a number of yield factors from data obtained at 500° C, concerning coals varying in rank from lignite to high volatile bituminous (22). Yield factors were the dependent variables, and various factors of the proximate and ultimate analyses, such as heating value (Btu), fixed carbon (FC), oxygen (O_2), hydrogen (H_2), and carbon to hydrogen ratio (C/H_2), were used as the independent variables. Correlation coefficients were found for combinations of from one to five of the independent variables. Equations were developed on an m.a.f. weight-percent basis for yields of: char; tar plus light oil; gas; volume of gas; and heating value per cubic foot of product gas. All values for gases were reported on an oxygen-and nitrogen-free basis. Equations included from one to three factors of proximate and ultimate analysis and heating value of the coal in Btu's as independent variables.

A literature survey of carbonization work done in other countries failed to reveal prediction equations for any component of product yield excepting char or coke. A formula was developed by investigators in India for predicting coke yields from the proximate analysis of coal, based on a statistical analysis of pilot-plant and full-scale plant data. Also developed were prediction equations for coke indices and shatter tests (10). Russian scientists investigated char yields obtained from 2.5 kilogram charges in perforated iron cylinders, surrounded by the same blends as in the cylinders. A chain of similar cylinders was extended horizontally across the inside of a coke oven, from one wall to the other. Regression analysis gave a multiple correlation coefficient (R) of 0.96, and the following equation:

$$C = 94.92 - 0.84\ VM\ (\text{dry basis}) + 7.7\ H_2\ (\text{m.a.f. basis})\ (33).$$

A Bolivian investigator from the National Institute of Carbon Information carried out a series of tests in a battery of industrial coke ovens, to develop a formula suitable for predicting char yields from high-volatile coals. The prediction equation he developed was:

$$C = 84.7 - 0.346\ (VM);\ (28).$$

No data has been published to date on carbonization of North Central Province lignites that attempted to correlate product yields with carbonization temperatures from 500° to 1,000° C.

CHAPTER II

APPARATUS AND CALIBRATION

USBM Assay Carbonizer

The carbonization units were essentially the USBM assay carbonizers developed at the Denver Station. Slight modifications were made because of operational difficulties encountered in preliminary tests, including a volume of product gas from some tests at 750° to 1,000° C greater than the capacity of the two gasholders. Figure 1 is a sketch of the basic unit. The following slight modifications were made: a 75 ml. test tube, partially packed with glass wool and immersed in an ice bath, was attached after the original tar-mist trap "U" as a second tar-mist trap. Immediately following, a 12-inch, mercury filled, "U" tube manometer was added as a pressure release safety trap. Safety trap "K" at the end of the absorption train was replaced with a "U" tube filled with calcium chloride. The automatic pressure regulator was not used for any of the tests. All pressure regulation was done using hand operated needle valves. The bellows-type, product gas mixing pump was replaced with an automobile fuel pump operating at 120 strokes per minute. A 34.41-liter stainless steel gas bottle provided additional capacity for product gas for tests where the total capacity of the original gasholders, 33 liters, was exceeded. An oil-sealed mechanical

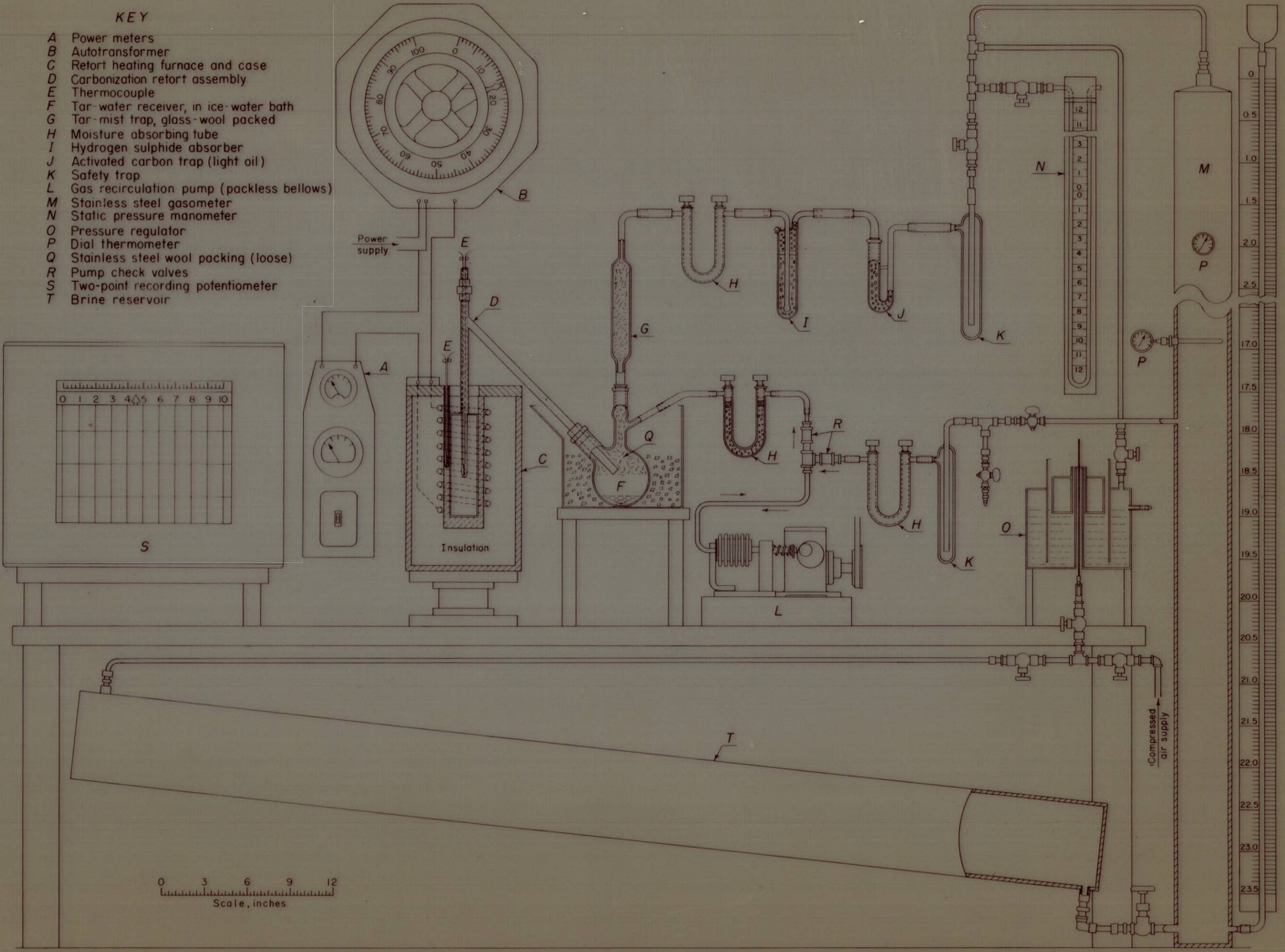


Fig I Precision carbonization assay apparatus.

vacuum pump served to remove air from the stainless steel bottle, to less than 1 mm of pressure, absolute, before collecting carbonization gases.

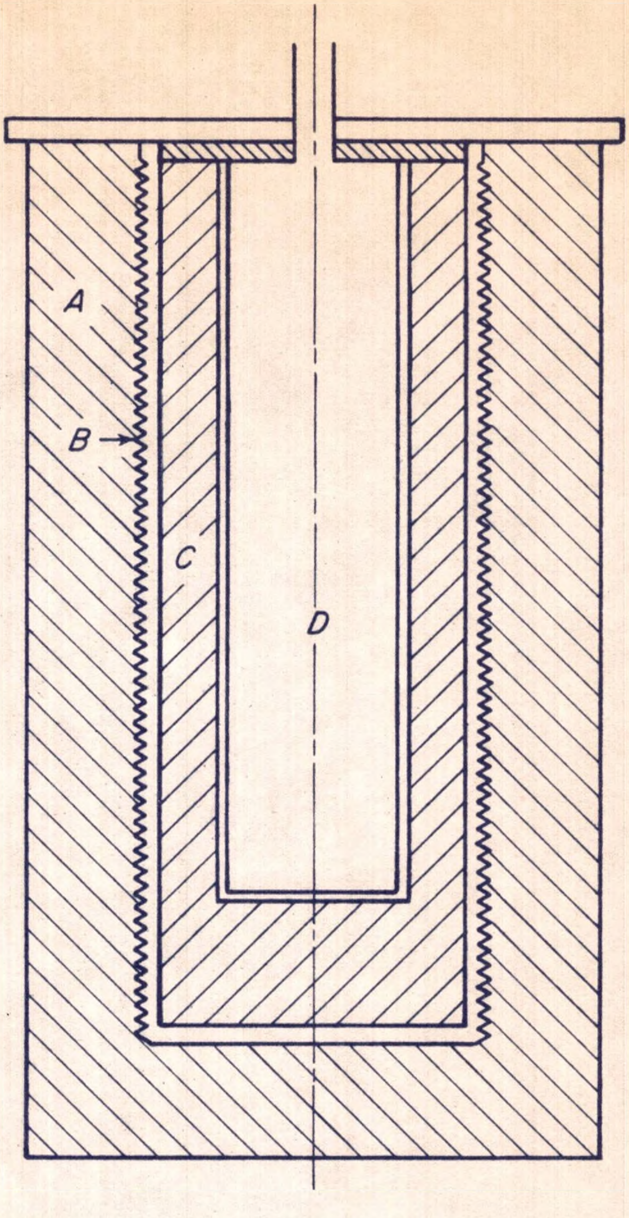
A detailed description of the apparatus used, other than the changes mentioned above, is listed on pages 5-10 of USBM Bulletin 530 (11). For light oil collection, approximately 11 grams of activated charcoal is used instead of the 25 mentioned in USBM Bulletin 530. This modification was inaugurated at Denver because of the use of an improved light oil trap which has greater efficiency.

Carbonization furnaces

Two furnaces were required to cover the planned range of temperatures. Figure 2 shows a cutaway view of the general construction of both furnaces. The major differences between the high- and low-temperature furnaces were in the increased size and capacity of the heating elements, and in the greater amount of "celite" insulation around the alundum core in the high-temperature furnace. In addition, the retort and thermostatic cylinder (heat sink) were constructed of stainless steel for the high-temperature and of carbon steel for the low-temperature furnace.

Temperature recorders

A separate Brown Electronik four point recorder was used to record the external and internal temperatures of each furnace. A recorder with a temperature range of 0° to 1,000° C and a printing cycle of 2 minutes was used for the 500° C furnace, while the high-temperature furnace recorder had a range of 0° to 2,400° F and a printing cycle of 8 seconds.



A Celite insulation
B Threaded alundum core 3" id x 9$\frac{1}{2}$" deep
C Stainless steel heat sink
D Stainless steel retort 2" od x 8" long

Fig 2 Assay retort heating furnace.

Gas analyzers

An Orsat-type analyzer (1) was used for most product-gas samples. A Burrell precision gas analyzer, build-up model with mercury as the confining liquid, was used to analyze duplicate gas samples from several tests. Gas analyses from the latter unit were used for calculations of yields for several tests when a negative value for ethane was obtained using the Orsat-type analyzer.

Balances

An Ainsworth, chainomatic, analytical balance, graduated in 0.1 mg divisions, was used to weigh the calcium chloride, hydrogen sulfide, and light oil traps. A Fisher double-pan scale, graduated in 0.1 gram divisions, was used to weigh the retort, tar-water trap, tar-mist traps, lignite charges, and xylene moisture samples.

CHAPTER III

EXPERIMENTAL PROCEDURES

The experimental procedures used generally followed those outlined in USBM Report of Investigation 5383 (14). Deviations from and additions to those procedures, deemed necessary in order to accomplish the objectives of the present tests, are explained in this section.

Preparation of Samples and of Charges

Approximately 350 pounds of freshly-mined lignite, crushed to a 3-inch by 0 size, was received in sealed 55-gallon steel drums from each of four mines. Approximately 200 pounds of lignite arrived from the fifth mine (Velva) in a sealed cylindrical cardboard carton. The total amount of lignite from each mine was separately crushed to minus one-half inch by passing through a hammermill, and then riffled into two approximately equal portions. One portion was sealed in heavy plastic bags, and stored as a reserve supply inside sealed steel drums. The second portion was recrushed to minus one-eighth inch. Because some of the lignites were more friable, there was some variation in the amount of crushed -20 mesh material from different mines.

The gross sample of minus one-eighth inch raw coal from each mine was hand-riffled into a number of approximately equal 600 to 700 gram portions. One sample per mine of "as-crushed" lignite was sent to the Coal Analysis Section of the Bureau of Mines at Pittsburgh, for proximate and ultimate analysis. The remaining samples were stored in tightly-sealed mason jars at a temperature of approximately 65° F (±5° F). A xylene moisture determination was made at the Grand Forks Coal Research Station from a sample of raw lignite from each mine, within a few days of the date of crushing to minus one-eighth inch. These initial xylene moisture determinations were then used as the basis for air-drying the lignite charges to the desired predetermined levels, i.e. 15, 20, 25, 30, and 35 percent moisture, respectively.

Adjustment of Moisture Content of Charges

Samples were placed in tared aluminum drying pans (13" x 9" x 2"), weighed to the nearest 0.1 of a gram, and air-dried at 35° to 40° C in a drying oven provided with a blower. When the weight of lignite and pan approached a precalculated weight corresponding to the desired moisture content, drying was completed at room temperature in the laboratory. A magnet, attached to the end of a single beam scale with 0.1 gram divisions, actuated an alarm buzzer when the desired weight was reached.

The partially dried sample was passed through a riffle splitter with three-eighth inch wide flutes, each half placed in separate pint jars, and purged with argon for 2 to 3 minutes prior to being sealed for storage. Argon, an inert gas approximately one-third heavier than air, appeared to be the best choice for both purging and maintaining an inert atmosphere in the jars of partially dried lignite, in order to minimize oxidation during storage.

All samples were stored in a basement room, where the ambient temperature varied from 55° to 70° F. It later became necessary to air-dry most of the reserve one-quart samples of "as crushed," minus one-eighth inch lignite. No differences were noted between product yields for samples dried in December, 1965, and those dried as late as May, 1966.

Operational Procedures

Lignite charge and samples

For each test, a 250 to 350 gram portion of minus one-eighth inch partially-dried lignite was used. This lignite was mixed by hand tumbling within the sealed storage jar, and riffled until the required portions were obtained for the retort charge, the xylene moisture sample, and the sample for proximate and ultimate analysis. Both the coal and char samples for proximate and ultimate analysis and heating value were mailed to Pittsburgh in double plastic bags, after the bagged samples had been well purged with argon. For most tests, the mass of the coal charge was within ±0.5 gram of the designed weight, although the charge variation for one test was -1.4 grams. The mass of charge was varied from 120 to 160 grams, in increments of 10 grams. The xylene moisture coal sample was approximately 50 grams while the remaining coal, 40 to +100 grams, was used as the Pittsburgh sample.

After the carbonization unit had been completely assembled, it was pressure tested for leaks under a vacuum of 8 to 12 inches of water. If a pressure rise of more than 0.5 inch of water occurred within 8 minutes, the system was checked for leaks until the leak check was satisfactory.

Carbonization temperatures and heating rate

The USBM assay carbonizer was operated essentially according to the procedure outlined by Goodman and associates (12). An average heating rate of approximately 8° C per minute was maintained for all tests, from the time of initial heat input until the external thermocouple had reached the selected carbonization temperature. The temperature of the external thermocouple was then held at the selected temperature for one hour, at which time the carbonization was considered to be essentially completed. Carbonization temperatures selected were 500; 625; 750; 875; and 1,000° C to facilitate statistical analysis of the data.

Analysis of product gases

At the end of each test the product gases were thoroughly mixed by recycling through the system with the recycle gas pump for from 10 to 30 minutes, depending on the volume of gas produced. The 3 minutes of mixing indicated by Goodman and associates (16) was found to be very inadequate for homogeneous mixing of product gases from any of the tests. Two gas samples were collected from each test in 250 ml gas sample bottles, by displacing a saturated solution of sodium chloride under a positive pressure of several inches of water. Most gas samples were analyzed using an Orsat-type gas analyzer.

Operational difficulties and modifications

During carbonization tests made at 750° C, it was first noted that some partially carbonized lignite (up to 10 percent of the weight of coal charged) was carried into the tar-water trap by a sudden rapid release of the carbonization gases. This char carry-over was caused by one or more of several factors, including: too small an annulus in the retort vertical offtake tube; condensation of higher temperature tars in cooler parts of both offtake tubes; or too many fines in the lignite charges from some mines. Tar condensation in the offtake tubes caused temporary plugging, which required a build up of gas pressure in the retort to open. This sudden release of a large volume of gases caused varying amounts of fine char to be carried out of the retort. Some of the char stuck to the tar in the offtake tubes, increasing the tendency to plug.

Fine coal carry-over occurred at internal thermocouple temperatures of 280° to 595° C, with 288° to 425° C being the critical temperature range, which is also the range of most rapid gas evolution. Once char carry-over was noticed, the liquid from the tar-water trap from each succeeding test was vacuum filtered through a Buchner funnel, after completion of the xylene-benzene distillation (8). The flask was rinsed several times with small volumes of acetone to remove char particles. When vacuum filtering and weighing of char carry-over was started, the filtered char was only air-dried before weighing. After several additional tests, it was decided to record weights of the filtered char after air-drying, and after oven-drying at 105° to 110° C for approximately 1 hour. The oven-dried weight averaged approximately 90 percent of the air-dried weight for all tests where both weights were recorded. Most of the char carry-over occurred in tests where the maximum carbonization temperatures were 625° C or higher, but it occasionally occurred at 500° C.

Corrective measures

The internal thermocouple well was decreased to three-sixteenths inch OD and both retort offtake tubes increased to one-half inch ID. Heat loss was considerably reduced by increasing the insulation on top of the retort and on the gas offtake tubes. Both of these factors reduced char carry-over in subsequent tests. They reduced the amount of tar that condensed inside the offtake tubes, and provided larger areas in both offtake tubes for less restricted outflow of tar vapors and product gases.

Goodman suggested preheating high moisture coals in the retort at 100° C until the excess moisture has been driven off (17). Such a procedure was not practical for a series of tests in which moisture content of charge was a designated variable.

CHAPTER IV

DESIGN OF EXPERIMENTS

The Greco-Latin square is an experimental design in which there are four independent variables, arranged in a balanced block design. Greco-Latin "squares" of size _t_ do exist when _t_ is a positive odd integer greater than 1, or a power of a prime, or a number satisfying the relation: $t = 4k + 2, (k = 2, 3, \ldots)$ (39). The advantage of a Greco-Latin square design is that four factors can be tested with the same number of experiments required to test two variables. It also provides a residual or error term with sufficient degrees of freedom to give a reasonable critical value for "F" at the significance level selected. Usually, this design is used in screening variables to be tested for significant effects where there are a relatively large number of variables having possible significance.

A normal Greco-Latin square has limitations in that interactions and experimental error are both included in the residual term. It is most useful where interactions can be assumed to be small or nonexistent. These disadvantages can be avoided to some extent by replication of the basic design, to allow a sum of squares for replication and for interactions to be calculated. However, all interactions are not independent, but their existence can be inferred at the significance level selected. The usual restrictions for statistical design must be followed in terms of randomization (40).

Basically, the experimental design employed is an extension of a two-factor classification in which there are an equal number of rows and columns. Referring to the 5 x 5 balanced block design used for the present experimental series, two additional variables were superimposed on the two factor 5 x 5 arrangement, so that each of the 25 blocks contained a different combination of the four experimental variables. Each level of each factor appeared only once in each row and in each column. Temperatures were assigned as column factors, mines as row factors, moisture contents of charges as Latin letters, and weights of charges as Greek letters.

To prevent duplication of conditions between blocks, the variables were assigned blocks as shown in table 1. The Latin letters were arranged alphabetically, A through E, with A at the top of the first column, B at the top of the second column, and so forth. The Greek letters were arranged alphabetically, α through ϵ in each column, beginning with α in the first column. For columns two through five it was necessary to list the Greek letters alphabetically, beginning with the third letter from the previous column. Otherwise, each of the 25 blocks would not have had a different set of conditions. This balanced block arrangement was designed to provide the maximum available data from the minimum number of experiments. Performance of each test in duplicate was necessary to determine the magnitude and significance of the error difference between duplicates, and to test for interactions. Replication also increased the degrees of freedom for the error term.

TABLE 1

EXPERIMENTAL DESIGN OF GRECO-LATIN SQUARE

Row variable level	Column variable level I	II	III	IV	V
1	A α	B γ	C ε	D β	E Δ
2	B β	C Δ	D α	E γ	A ε
3	C γ	D ε	E β	A Δ	B α
4	D Δ	E α	A γ	B ε	C β
5	E ε	A β	B Δ	C α	D γ

Levels and coding of variables

	Temperatures, °C
I	500
II	625
III	750
IV	875
V	1,000
	Mines
1	Beulah
2	Velva
3	Peerless
4	Savage
5	Kincaid
	Xylene moisture content of charge, wt. %
A	15
B	20
C	25
D	30
E	35
	Weight of charge, grams
α	120
β	130
γ	140
Δ	150
ε	160

CHAPTER V

RESULTS AND DISCUSSION

Experimental Results

Experimental data

Including preliminary and rejected tests, a total of 79 assay carbonization tests were made at the 25 different test conditions outlined in table 1. Performance of additional tests in excess of the required 50 were necessary because of operational difficulties resulting in low material balances and unusual variations in various yield components between duplicates for some tests. When excessive variations occurred between duplicate tests at any level for one or more of the six components of yield, the tests were repeated. The yields of products of carbonization, proximate and ultimate analyses of lignite charge samples, proximate analyses of char samples, product gas analyses, and other pertinent data from each of the 50 selected tests are listed in table 1, appendix C.

Variations occasionally occurred between product gas analyses from duplicate tests, especially for carbon dioxide, methane and ethane. The largest variation in carbon dioxide content between duplicate tests occurred at 1,000° C using Peerless lignite.

Statistical Analysis

Fifty tests, representing 25 different test conditions in duplicate, were selected as being satisfactory for statistical analysis, based on material balance (usually within ±0.5 percent), known quantity of lignite carry-over to the tar-water trap, and a reasonable agreement of gas analyses between duplicate tests. Table 2 indicates the general scheme for analysis of variance (34). Preliminary calculations showed that, excepting for the minor factors of water of formation and hydrogen sulfide (H_2S), the interactions effect was not significant at the 95 percent confidence interval compared to the error term having 8 and 24 degrees of freedom for the critical F value. Consequently, the interactions term was pooled with the error (residual or unassigned variance) term to give the reported error factor with 32 degrees of freedom, and the pooled error term was used as the denominator for subsequent calculations of F values. The replication (duplication) factor was also not significant, but was not pooled with the error term so that an estimate of the standard deviation for replication could be calculated. The nonpooling of the replication factor was not important in the total scheme of statistical inference, as the replication effect was small, and the increase from 32 to 33 degrees of freedom for the error term would not appreciably reduce either the critical or calculated F value. In each instance, the calculated F value is the ratio of the mean square for the factor considered to the mean square of the error factor. For the four main factors it would be compared to the critical F value at the selected level having 4 and 32 degrees of freedom (26).

TABLE 2

ANALYSIS OF VARIANCE FOR GRECO-LATIN SQUARE DESIGN

Source	Sum of squares	DF	MS	Critical F 0.05	Critical F 0.01	Est. MS
ine	$\frac{\sum_{1}^{5}(\text{Mine totals})^2}{10} - \frac{(\sum Xijk)^2}{50}$	4	SS/DF	2.674	3.982	$\sigma_e^2 + 10\,\sigma_\alpha^2$
emper- ture	$\frac{\sum_{1}^{5}(\text{Temp. totals})^2}{10} - \frac{(\sum Xijk)^2}{50}$	4	SS/DF	2.674	3.982	$\sigma_e^2 + 10\,\sigma_\beta^2$
oisture n charge	$\frac{\sum_{1}^{5}(\text{Moist. totals})^2}{10} - \frac{(\sum Xijk)^2}{50}$	4	SS/DF	2.674	3.982	$\sigma_e^2 + 10\,\sigma_\gamma^2$
eight of harge	$\frac{\sum_{1}^{5}(\text{Weight totals})^2}{10} - \frac{(\sum Xijk)^2}{50}$	4	SS/DF	2.674	3.982	$\sigma_e^2 + 10\,\sigma_\Delta^2$
eplicate	$\frac{\sum_{1}^{2}\left(\sum_{1}^{25}\text{Reps. totals}\right)^2}{25} - \frac{(\sum Xijk)^2}{50}$	1	SS/DF	4.152	7.51	$\sigma_e^2 + 25\,\sigma_{rep.}^2$
rror	Difference	32	SS/DF			σ_e^2
otal	$\sum_{1}^{50}(Xijk)^2 - \frac{(\sum Xijk)^2}{50}$	49				

Analysis of variance

Tables 1 through 9, appendix D, give results of the analysis of variance for each of the six carbonization yield components, tar plus light oil and heating value of oxygen and nitrogen-free product gas per pound of lignite charge, all on an m.a.f. basis, and heating value of oxygen- and nitrogen-free product gas in Btu's per cubic foot. The four independent variables and the replicates effects were tested at both the 95 and 99 percent confidence intervals (0.05 and 0.01 α levels). Temperatures were significant at the 99 percent interval for eight of the nine yield factors, but were not significant at the 0.01 level for water of formation. Mines were significant at the 99 percent confidence intervals for all nine factors tested. Xylene moisture content of lignite charge was significant at the 99 percent confidence interval for weight percents of light oil and H_2S. Weight of charge was not significant for water of formation and heating value of product gas per cubic foot, but was significant for dry tar and H_2S at the 95 percent confidence interval. Weight of charge was significant at the 99 percent confidence interval for the other five yield factors tested.

The analysis of variance indicates that the temperature level, mine, and weight of charge carbonized would significantly, and usually highly significantly (0.01 level), influence the results of carbonization of lignite in the USBM assay carbonizer. Both temperature and source of lignite had been assumed to be critical independent variables, an assumption confirmed by the present test series. In previous work, weight of charge and initial moisture content had been assumed to have an insignificant influence on carbonization yields. The present work indicates that weight of lignite charged to the USBM assay carbonizer does have a significant influence on the product yields, and should be controlled at some selected constant value; at least until this significance is reaffirmed or disproved by a subsequent series of tests, after adequate modifications have sufficiently reduced the weight of charge carried out of the retort. Essentially, the assumption that initial moisture content of charge does not appreciably influence the test data was confirmed, and this variable may be eliminated from consideration in additional assay work without introducing a significant error. However, temperature level, source of lignite, and weight of charge should be specified to obtain comparable results.

An indication of the extent of influence of different independent variables is given in table 3 in the text, where the estimated variance of the effect, σ_1^2, is given for each of several dependent variables (a high value indicates greater influence). For the dependent variables listed, the effect of temperature is generally several orders of magnitude greater than for the other independent variables. But, for yields of tar plus light oil, the mine effect is approximately four times greater.

In tables 1 through 9, appendix D, the relative magnitudes of the mean square values listed may be considered measurements of the importance of the independent variables. Their values indicate that the mine effect predominates for water of formation, H_2S, and heating value of product gas per cubic foot on an oxygen- and nitrogen-free basis, as well as for tar and light oil. Yields of char, and product gas, and heating value of product gas (oxygen- and nitrogen-free) per pound of lignite charge on an m.a.f. basis, are mainly affected by temperature variations. A much reduced effect on yields is caused by weight of charge, while replicates and moisture content effects are very small. Variance assigned to replication is so small in comparison to that associated with temperature level and mines that replication should not be required in subsequent investigations.

TABLE 3

VARIANCE OF PRINCIPLE YIELD FACTORS FOR SINGLE TEST[1/]

Source		(Weight percent)^2 m.a.f.			Heating value of product gas: (O_2 - N_2 free) [Btu/lb. coal, m.a.f.]^2
		Char	Tar + light oil	Product Gas	
Mines	σ_α^2	3.157	1.354	1.291	8,498.3
Temperatures	σ_β^2	17.191	0.331	22.179	1,619,991.4
Moistures in charges	σ_γ^2	0	0.063	0.092	0
Weights of charges	σ_δ^2	0.647	0.163	0.582	2,938.5
Replicates	$\sigma_{rep.}^2$	0.043	0	0	66.0

[1/] Calculated from estimated mean square.

The above analysis of variance indicates that for determination of prediction equations for carbonization yields, the equation should be multivariate, and include some function of temperature and of composition (source of lignite). The independent variable of charge weight should be considered, but in standard assay practice this factor would be specified at some constant value. Consequently, this factor can be neglected in a general prediction equation, although some of the scatter of data can be attributed to this factor.

Regression and correlation

All regression equations formulated were tested for values of multiple correlation coefficients and significance of each independent factor of the equation using an IBM 1620 digital computer, working on a multiple regression package program (9). Equations were tested separately for m.a.f. weight percent yields of char, tar, light oil, tar plus light oil, H_2S, product gas, and heating value of gas as dependent variables, and temperatures plus one or more factors of proximate and/or ultimate analyses of the lignite charges as independent variables. From the analyses of the lignites as charged to the retort, factors selected for testing in regression equations were: Btu per pound of charge, fixed carbon (F.C.), oxygen (O_2), hydrogen (H_2), carbon (C), sulfur (S), C/H_2 and O_2/H_2 ratios, all on an m.a.f. basis, and as-charged xylene moisture. Weight of charge was excluded from all product yield equations tested, despite its significance in the analysis of variance test for seven of the nine yield factors tested, for reasons previously stated.

Results of prediction equations

Table 10, appendix D, shows the results for a number of the regression equations having high correlation coefficients. Listed are the dependent (Yi) and independent (Xi) variables, the computed multiple correlation coefficient (Rm), the critical correlation coefficient at the 99 percent confidence interval (Rc), and the degrees of freedom available for the residual or error term (DF). Since the relation of product yield to temperature was not entirely linear, particularly within the range of 500° to 625° C (see figures 3 through 6), squared values of temperature and heating value (Btu per pound of coal, m.a.f.) of lignite charges were used in some equations. Squared and cubic values of other factors of lignite analyses, such as percentages of F.C., H_2, O_2, and C, were tried in developing some equations but results were not promising.

Equation quadratic with respect to carbonization temperature gave multiple correlation coefficients (Rm) of from 0.865 to 0.982 for all seven factors tested. Fixed carbon significantly affected the multiple correlation coefficient for char yield; heating value of lignite charge (Btu/lb, m.a.f.) and (Btu/lb, m.a.f.)^2 affected the tar plus light oil yield. All other analysis factors tested, including xylene moisture content of lignite charge, had little effect on the multiple correlation coefficients. In all instances, linear equations gave lower correlation coefficients than equations containing quadratic components for temperature alone or temperature and (Btu/lb) and/or C/H_2 ratio on an m.a.f. basis. All multiple correlation coefficients listed in table 10, appendix D, are considerably larger than the related critical correlation coefficient at the 99 percent confidence interval, indicating that the listed equations are highly significant.

Standard deviation

The residual standard deviation of the dependent variable (Y), after regression variance is removed, measures the unassigned or error deviation of the dependent variable from the estimated true mean value. The standard deviation values in table 10, appendix D, were calculated as the square root of the residual error variance for each equation, respectively. The ranges of standard deviations for each dependent variable listed in table 10, appendix D, which are significant at the 99.9 percent confidence interval were as follows:

Dependent variable	σ0.001
Char yield	±1.45 to ±2.60 wt. %
Tar yield	±0.91 to ±1.42 wt. %
Light oil yield	±0.27 to ±0.82 wt. %
Tar and light oil yield	±0.89 to ±2.33 wt. %
Product gas yield	±1.86 to ±2.11 wt. %
Heating value of gas	±224 to ±238 Btu

These standard deviations are considered relatively large, particularly for the heating values of product gas, but the variance assigned to the prediction equations are all highly significant. Undoubtedly all of the above deviations could be reduced if some operating difficulties were eliminated. Also, since all yield factors (excepting heating value of product gas) are essentially linear functions of carbonization temperatures from 625° to 1,000° C (see figures 3 through 6), development of regression equations, excluding data collected at 500° C, should give improved equations with better fit and only linear components. Use of a separate furnace, designed for low-temperature carbonization, for the 500° C tests may have introduced some bias. But, this possibility was not investigated (15).

Plots of values of dependent variables calculated from regression equations versus values obtained from experimental data generally indicated that, for yields of char, the 500° C tests gave calculated values somewhat lower than the experimental data, while the 1,000° C tests gave calculated values higher than the experimental data. For product gas yields

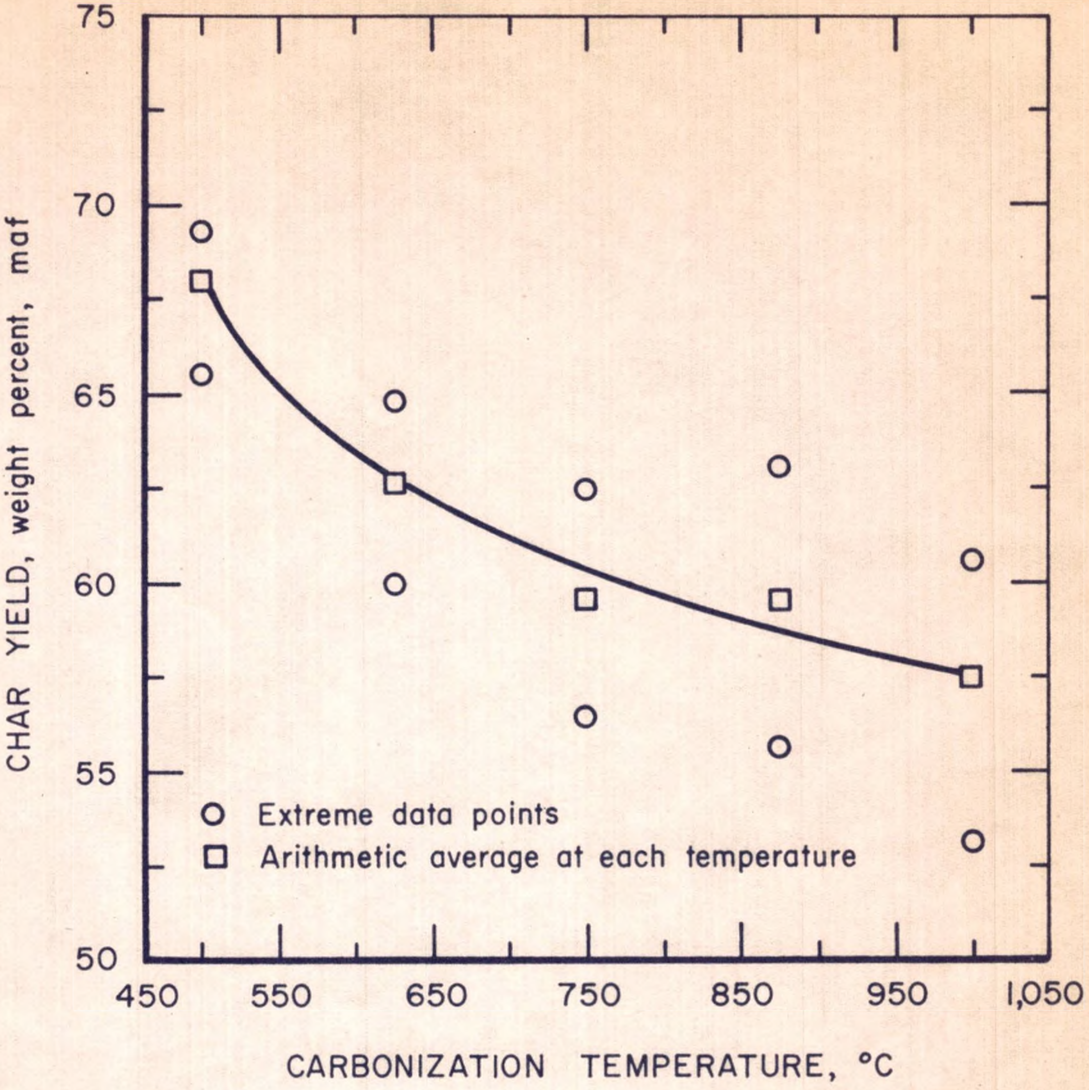


Fig 3 Char yield as a function of carbonization temperature.

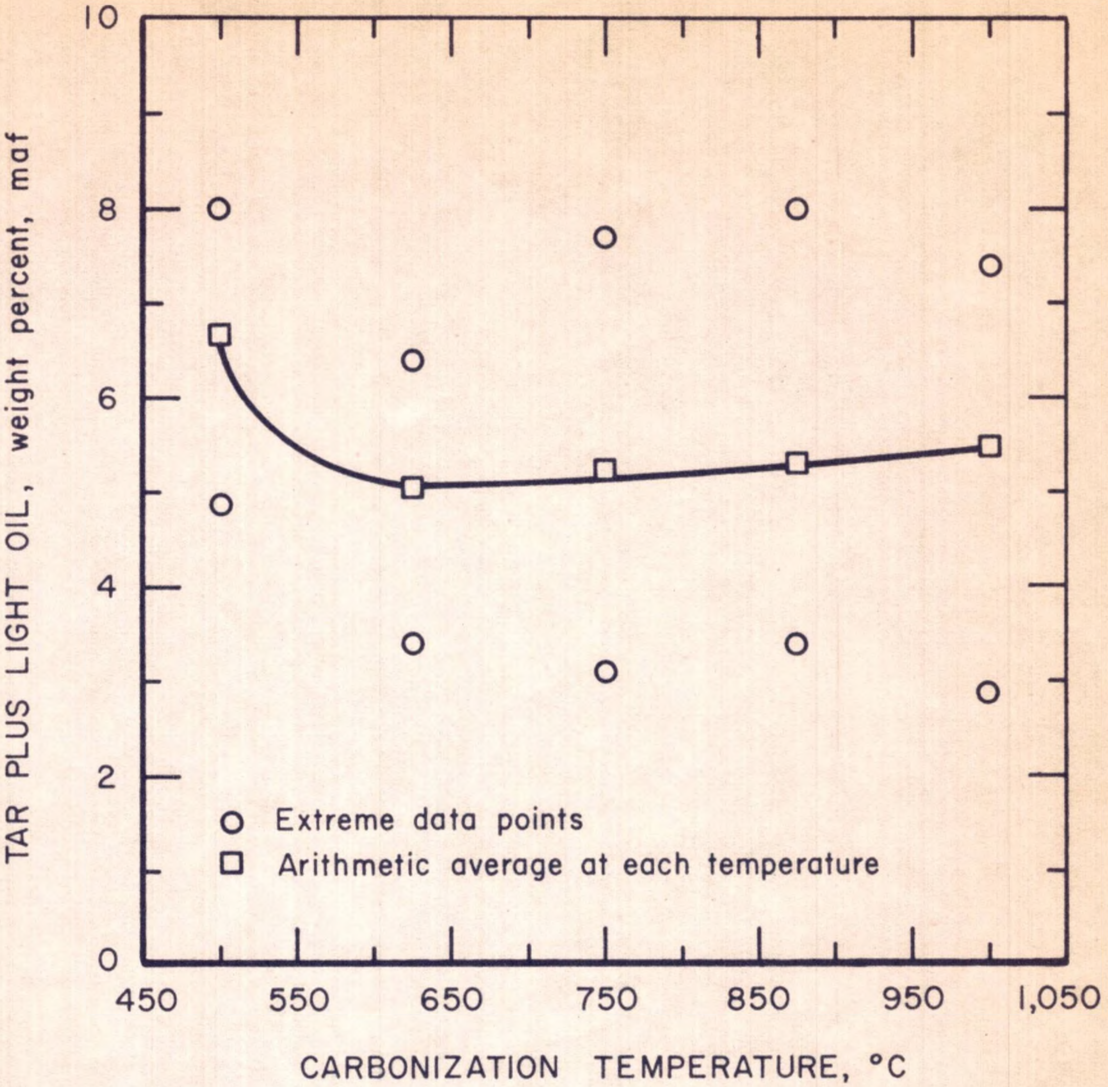


Fig 4 Tar plus light oil as a function of carbonization temperature.

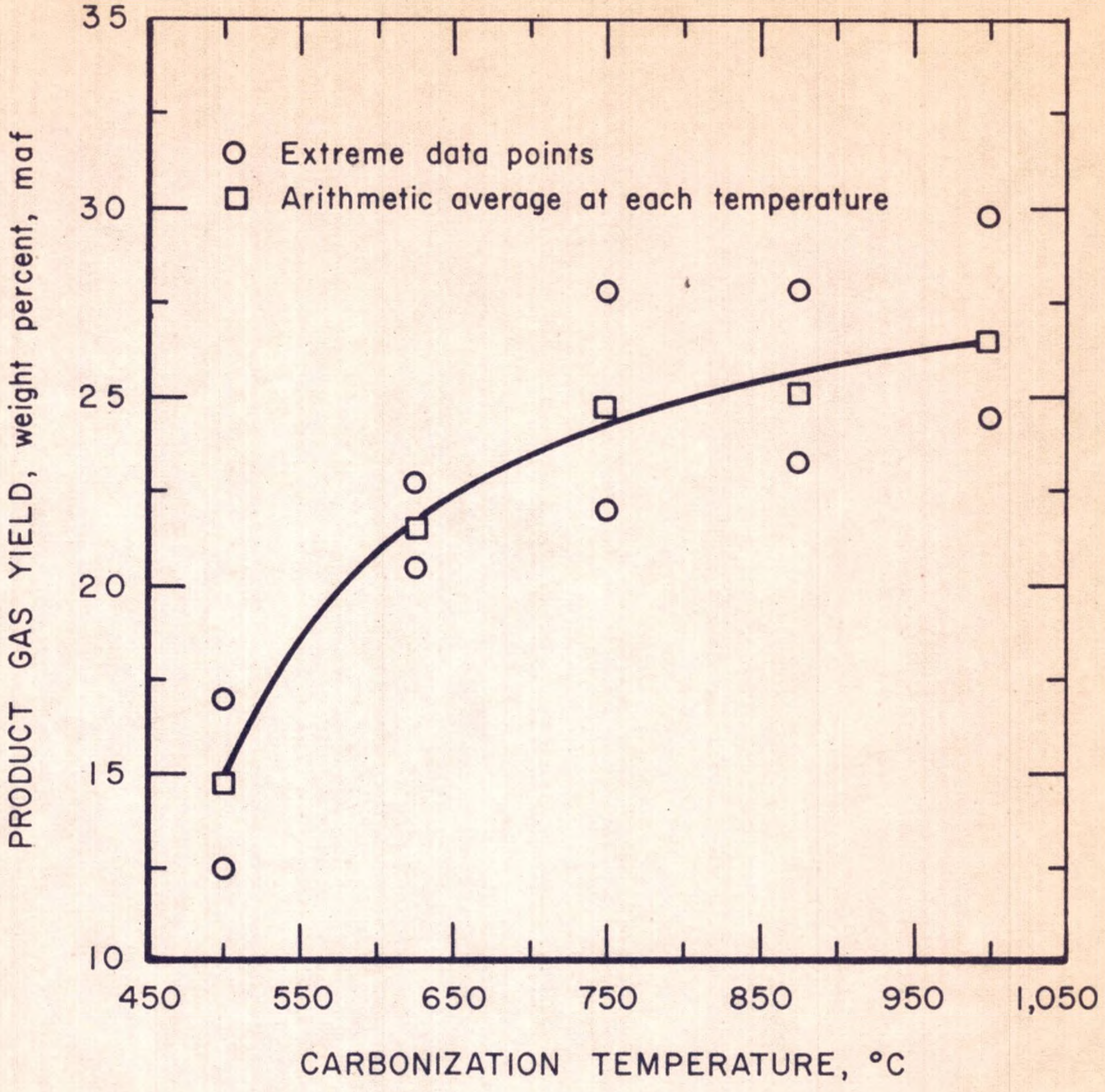


Fig 5 Product gas yield, O_2 and N_2 free basis, as a function of carbonization temperature.

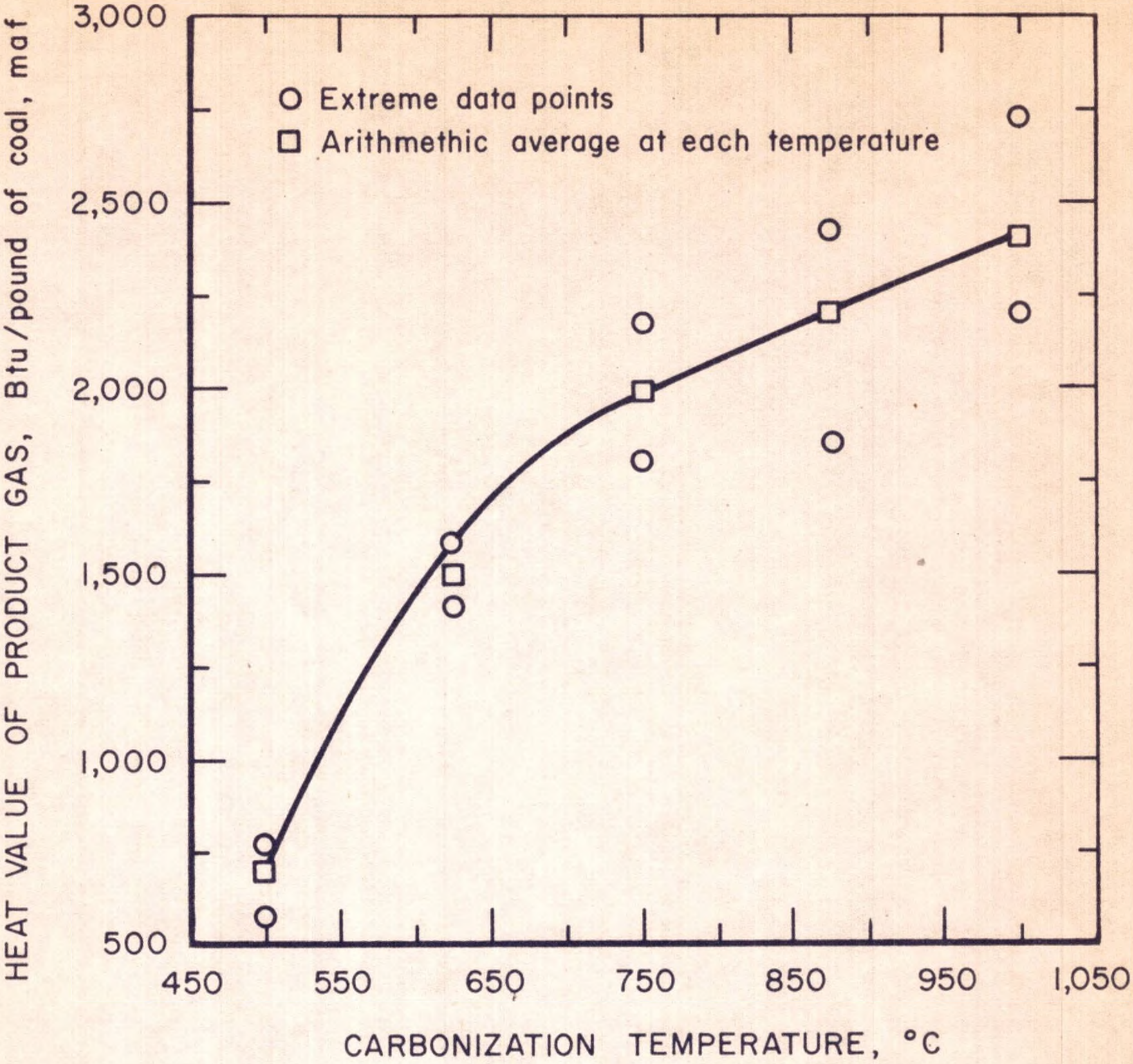


Fig 6 Heat value of product gas, O_2 and N_2 free basis, as a function of carbonization temperature.

and heating values, the 500° C tests usually gave calculated values higher than the experimental data while the higher temperatures gave calculated values lower than the experimental data. Calculated yields of tar plus light oil were generally lower than those from experimental data, and the plot exhibited more scatter than did other yield factors. These comparisons are evident from the plots in figures 7 through 14.

Regression equations containing a greater number of independent variables generally gave higher multiple correlation coefficients, and a slightly better fit for specific experimental data. However, a lengthy generalized multiple regression equation is undesirable because it is too cumbersome. Also, depending on the choice of additional independent variables, it may not give an improved general prediction equation. Such difficulties can be minimized by formulating prediction equations for dependent variables as functions of only the independent variables that cause a significant variation from the line of best fit (36).

Comparison of prediction equations

The following equation gave the best fit of the calculated values versus experimental data for char yield, weight percent, m.a.f. (Y_1), (see figure 9):

$$\text{Equation 3:}\quad Y_1 = 94.4 - 0.0951\,(T, ^\circ C) + 0.000050\,(T, ^\circ C)^2 + 0.530\,(F.C.) - 4.31\,(H_2)$$

Therefore, char yield is mainly a function of temperature and, to a lesser extent, of the fixed carbon and hydrogen contents of the charge. Table 4 lists comparative values for char yields at 500° C for experimental data and values calculated from equation 3 above, and from equations

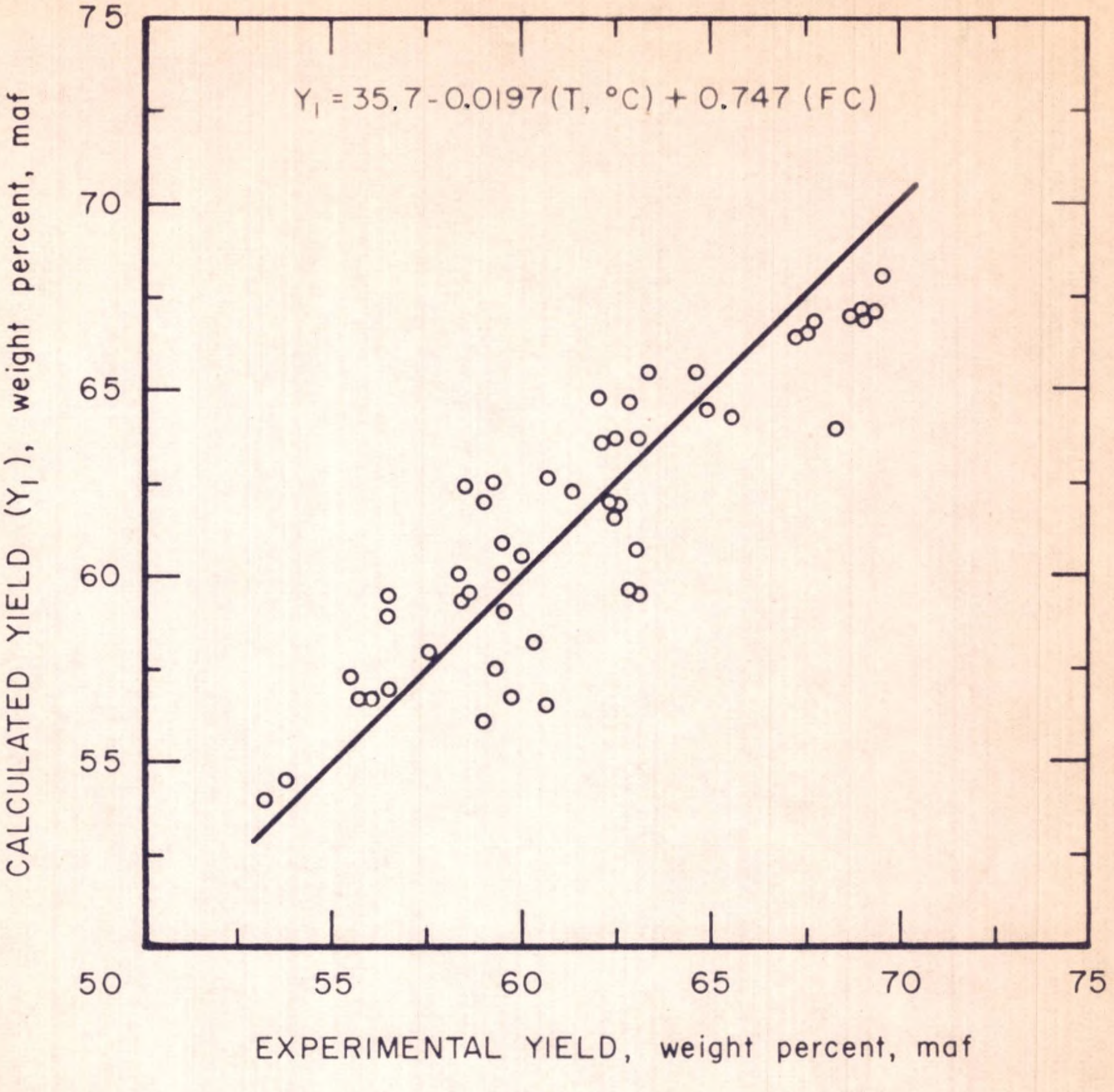


Fig 7 Calculated values (Y_1) versus experimental data for char yield.

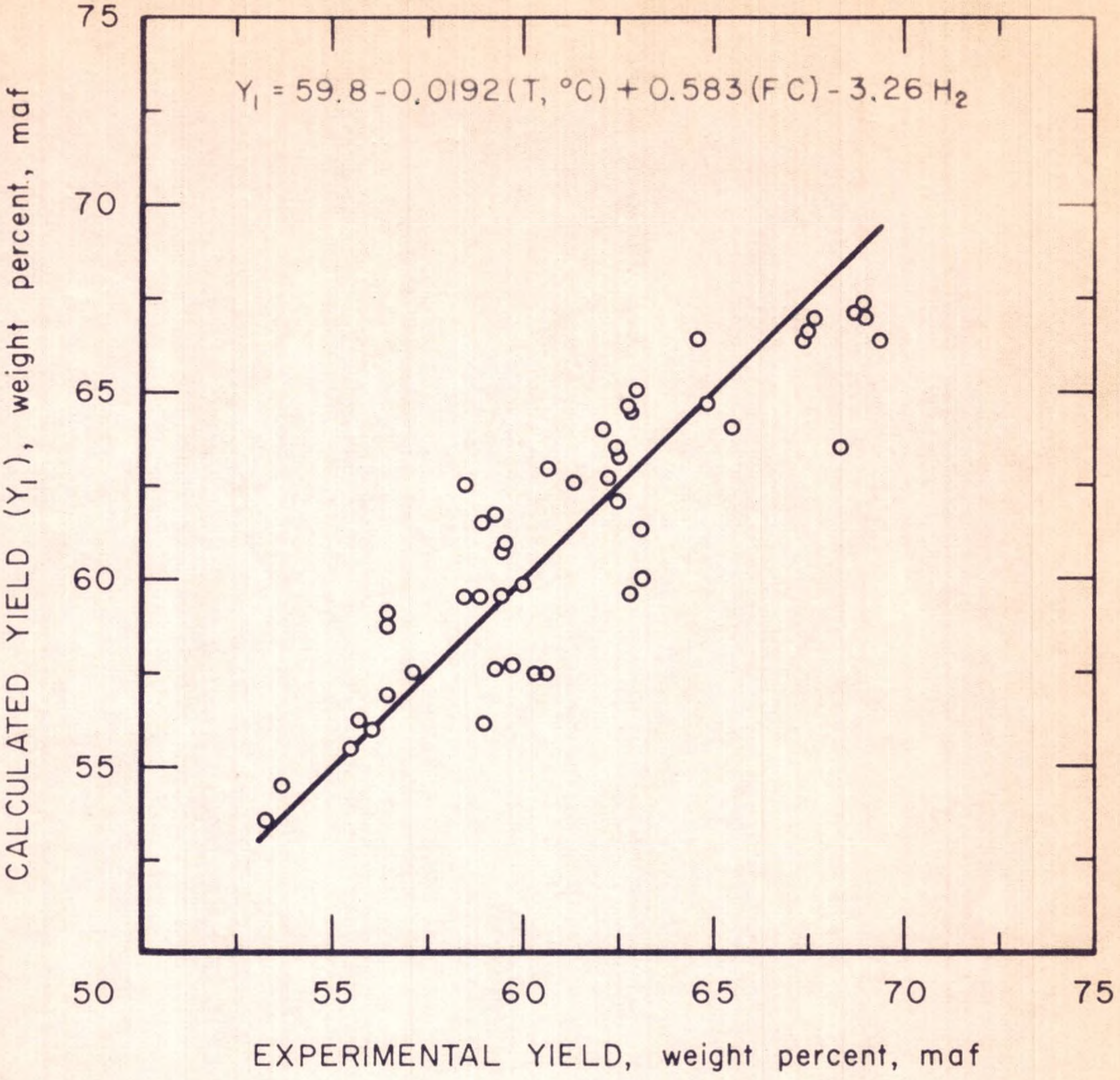


Fig 8 Calculated values (Y_1) versus experimental data for char yield.

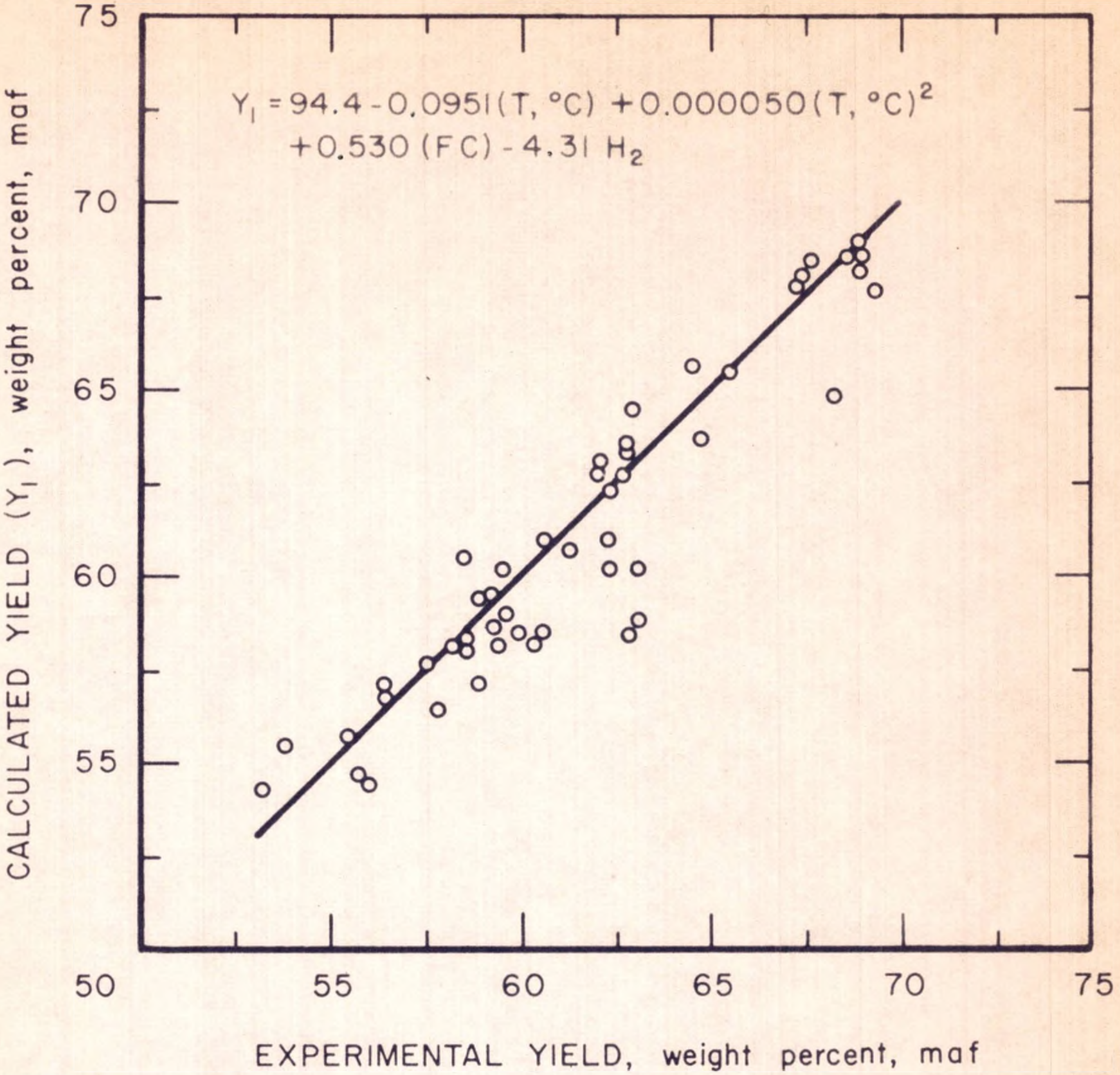


Fig 9 Calculated values (Y_1) versus experimental data for char yield.

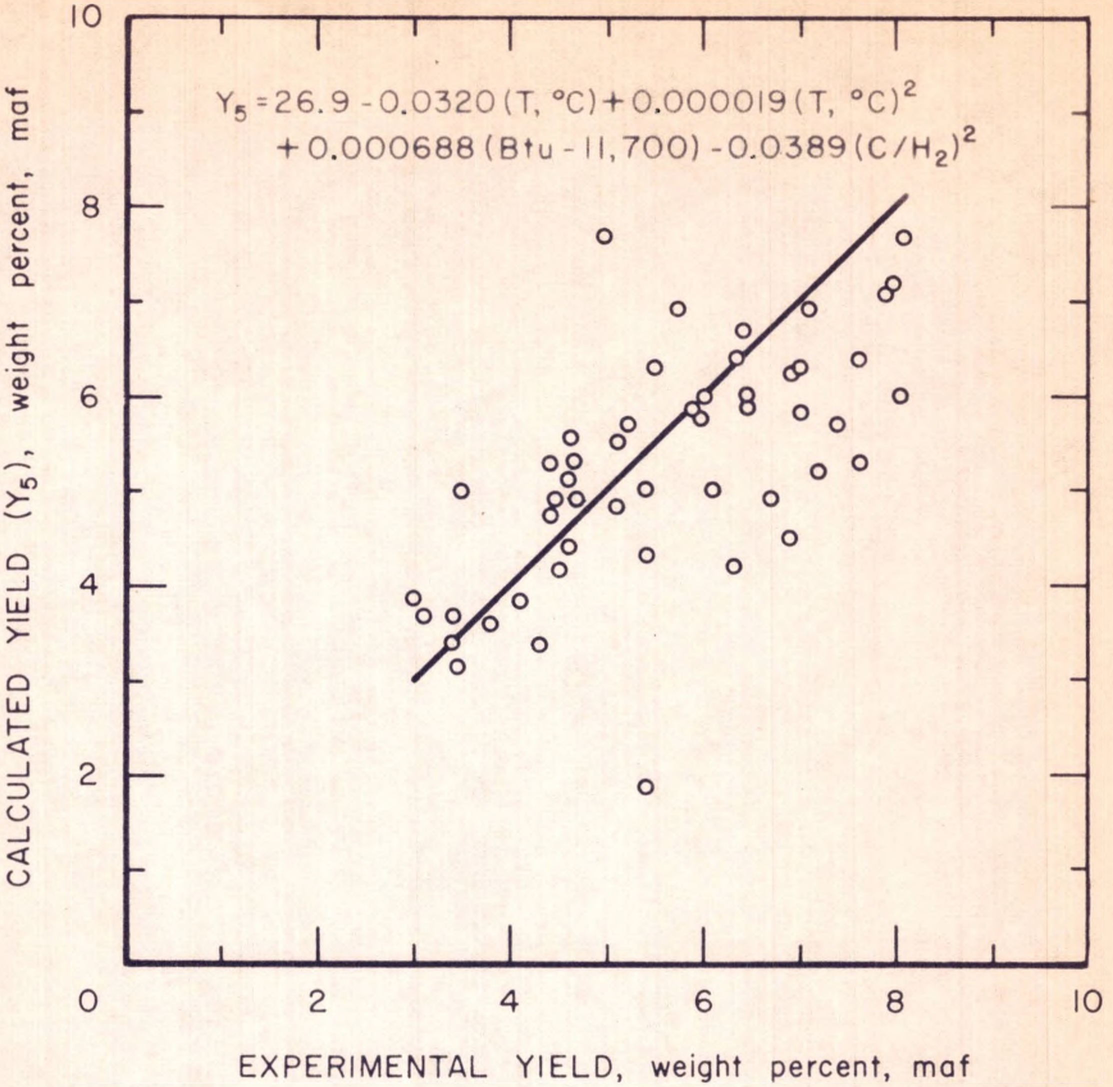


Fig 10 Calculated values (Y_5) versus experimental data for tar plus light oil.

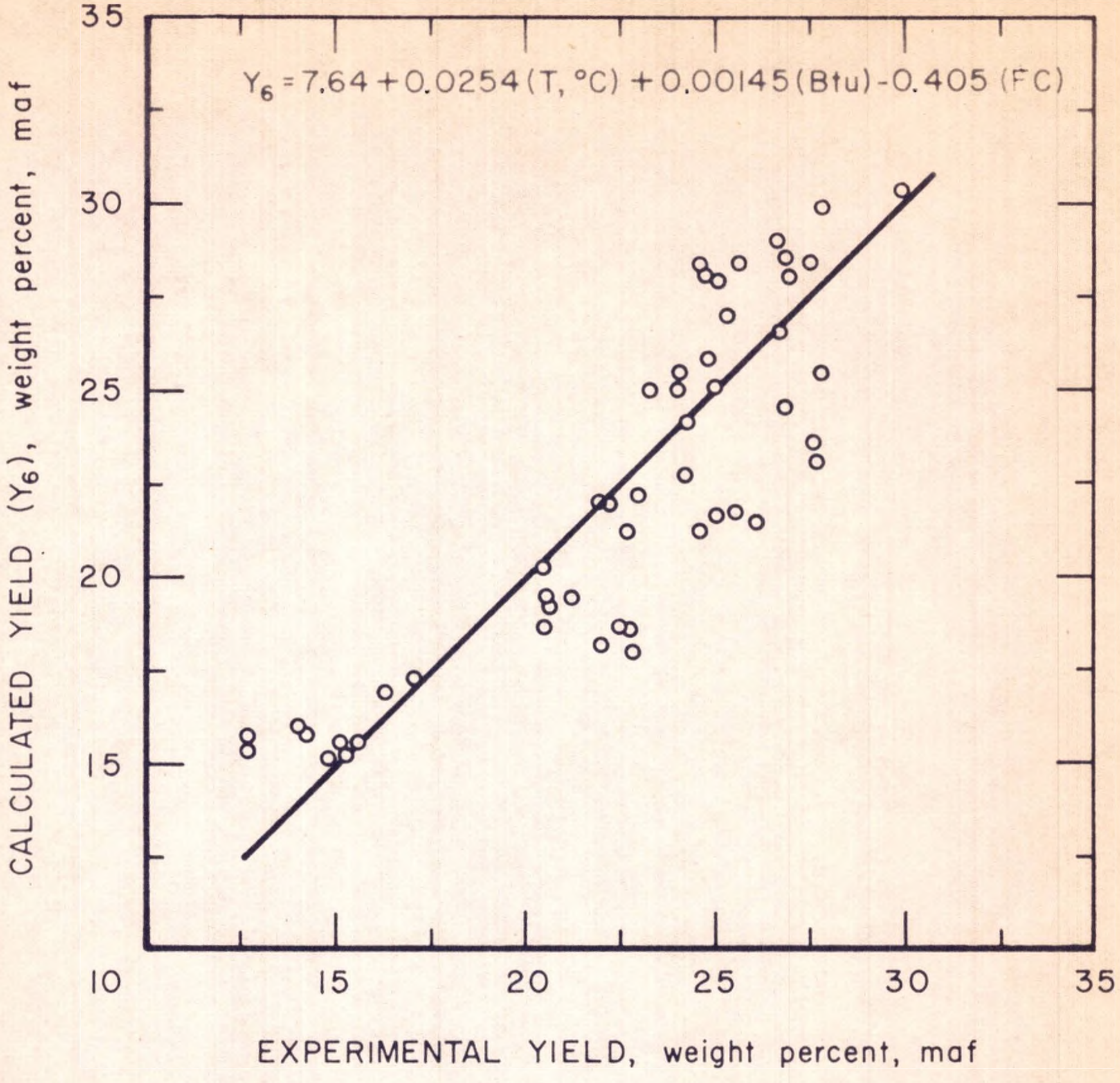


Fig 11 Calculated values (Y_6) versus experimental data for product gas yield, O_2 and N_2 free basis.

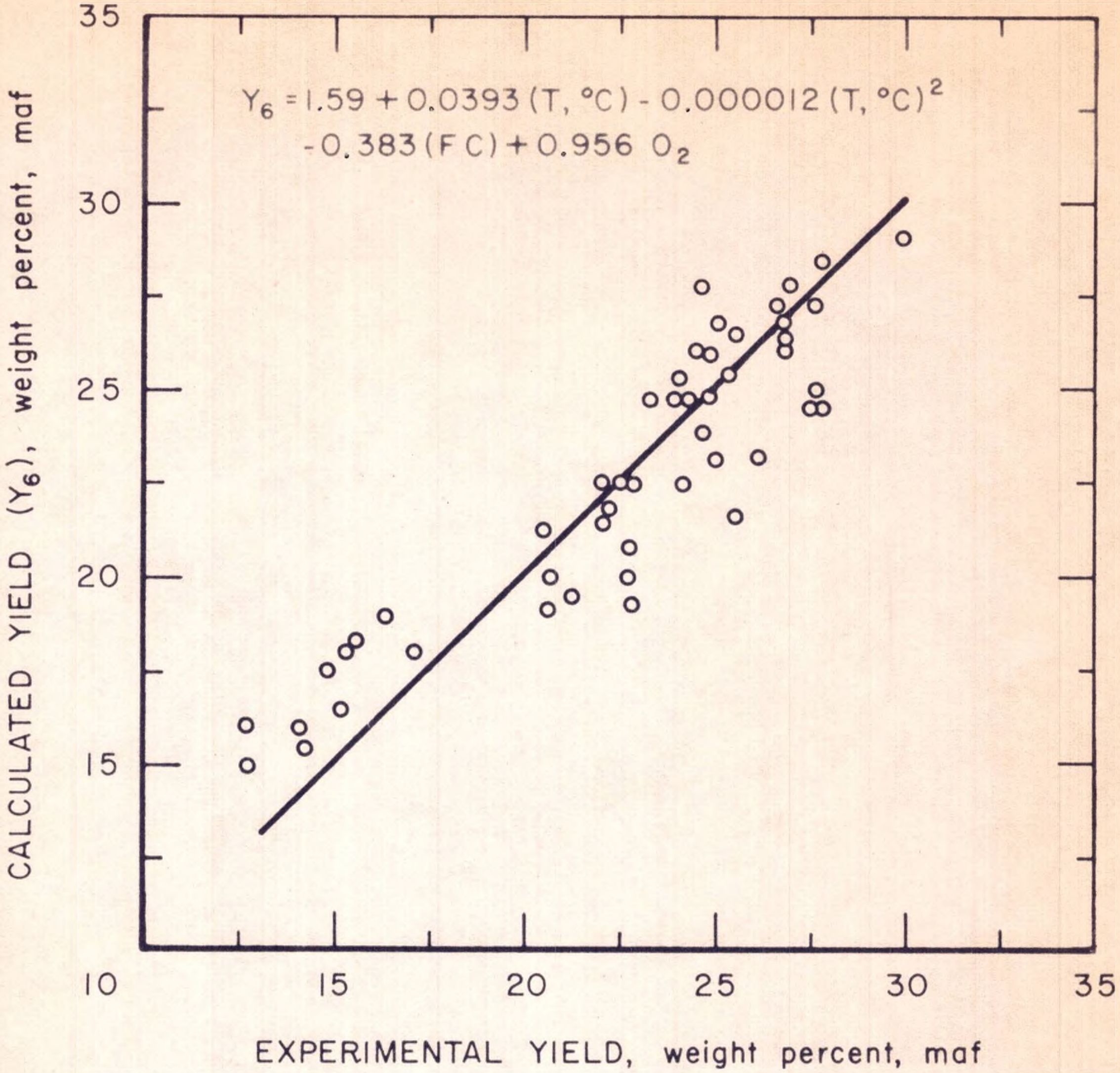


Fig. 12 Calculated values (Y_6) versus experimental data for product gas yield, O_2 and N_2 free basis.

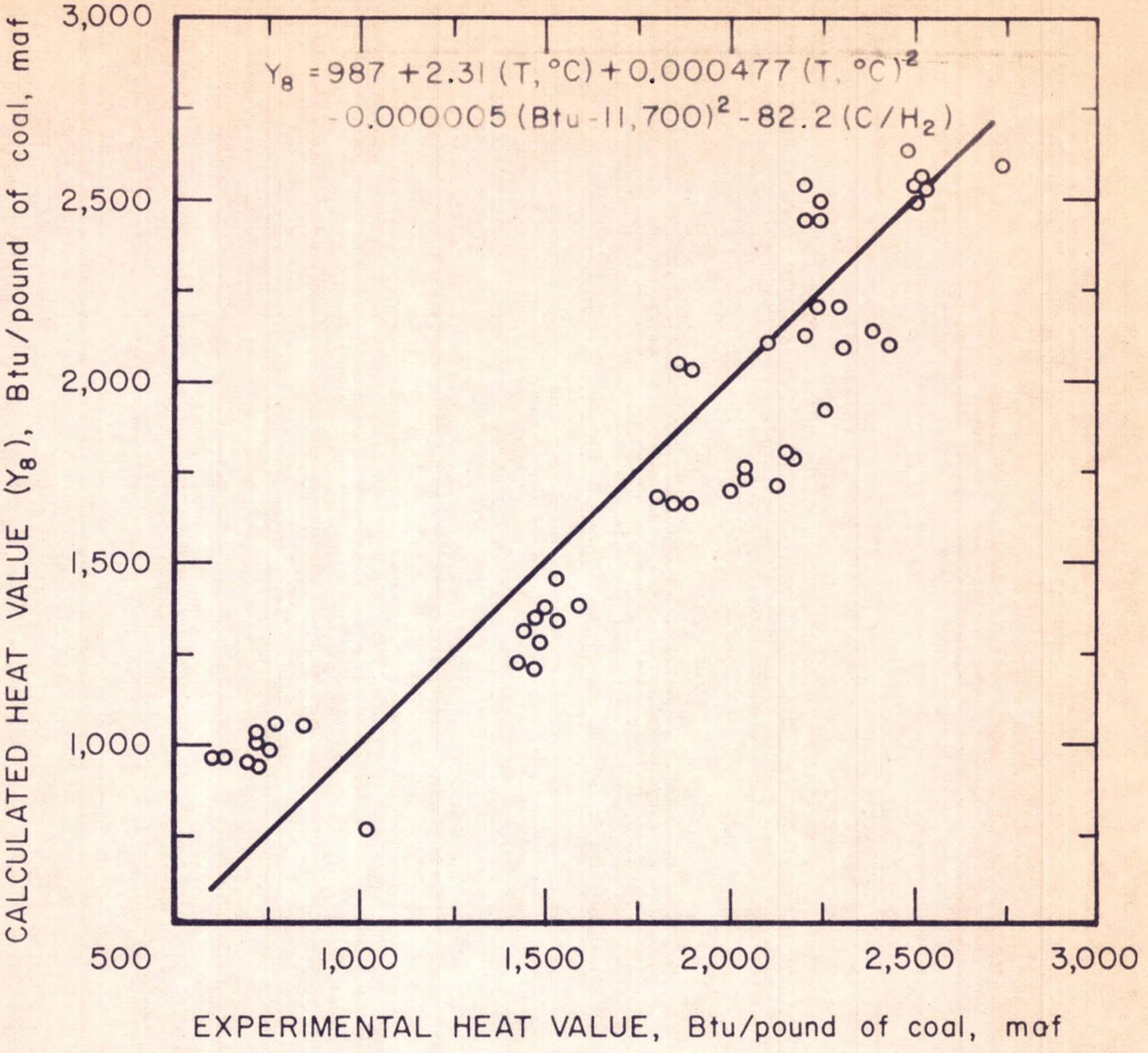


Fig 13 Calculated values (Y_8) versus experimental data for product gas heating values, O_2 and N_2 free basis.

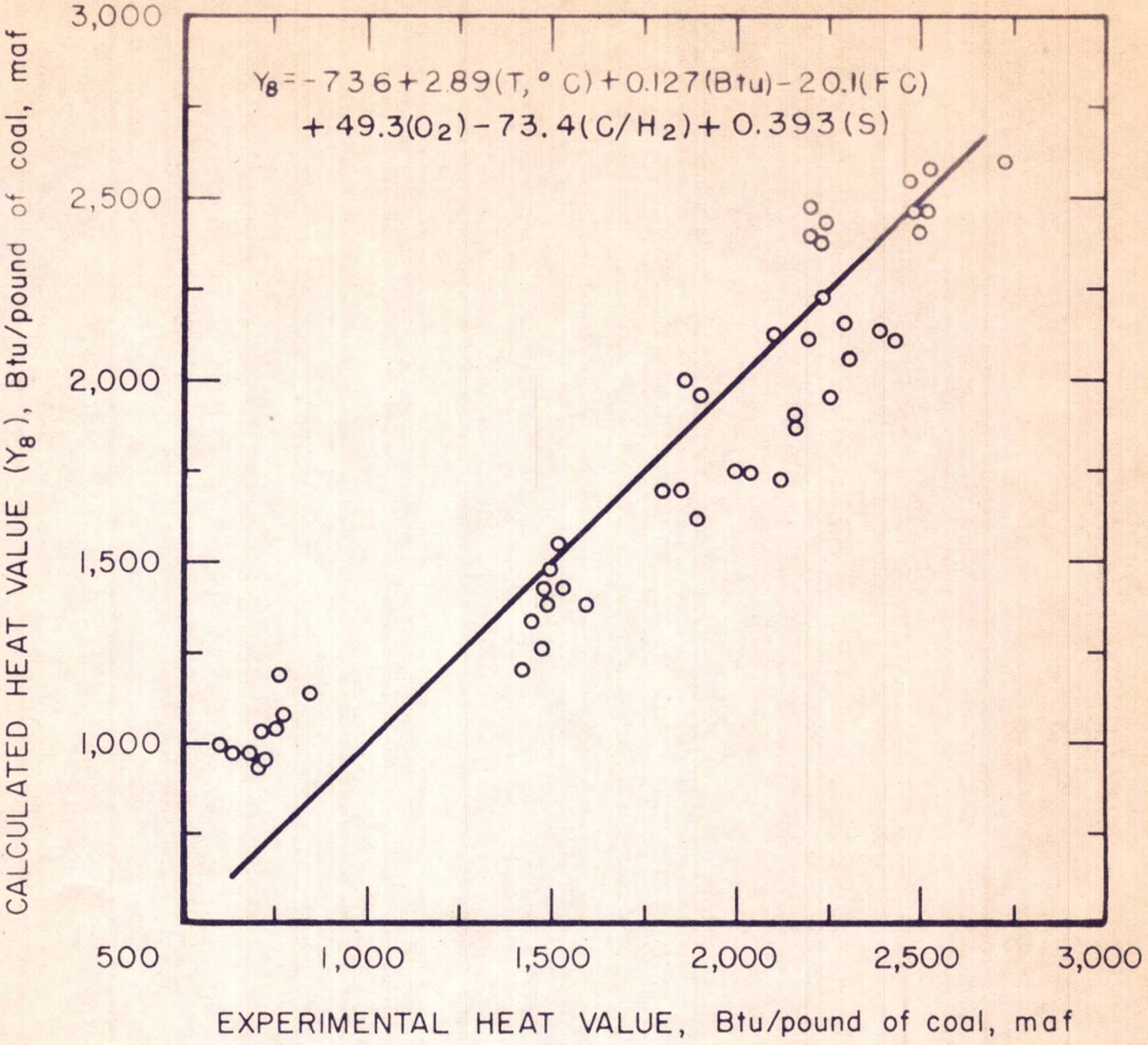


Fig 14 Calculated values (Y_8) versus experimental data for product gas heating values, O_2 and N_2 free basis.

TABLE 4

COMPARISON OF PREDICTION EQUATIONS WITH EXPERIMENTAL DATA AT 500° C

	Char, wt. %, m.a.f.						Tar+light oil, wt. %, m.a.f.			Product gas, wt. %, m.a.f.			
	Experimental	Equation No.					Experimental	Equation No.		Experimental	Equation No.		
Mine	Data	A	1	2	3	B	Data	C	4	Data	D	5	6
Beulah	67.8	70.5	66.8	66.9	68.3	62.3	6.96	7.11	6.30	14.2	12.3	15.9	15.5
Beulah	67.5	70.3	66.6	66.7	68.2	62.1	7.62	7.42	6.38	14.1	12.1	16.1	15.9
Velva	67.3	69.5	66.4	66.4	67.8	61.9	6.40	6.21	6.72	15.5	13.6	15.5	18.3
Velva	68.7	70.1	66.9	67.1	68.5	62.4	6.94	5.86	6.42	15.3	13.4	15.3	18.0
Peerless	68.3	67.2	63.9	63.5	64.8	59.2	4.95	9.29	7.66	17.1	12.8	17.3	18.0
Peerless	65.6	67.4	64.3	64.1	65.4	59.7	8.06	8.52	7.65	16.3	13.1	16.9	19.0
Savage	69.0	70.5	66.9	67.0	68.5	62.4	5.46	6.29	6.30	15.2	13.0	15.5	16.4
Savage	68.9	70.3	67.1	67.4	68.9	62.6	5.93	5.15	6.03	14.8	13.8	15.1	17.6
Kincaid	69.3	70.7	67.1	66.4	67.5	62.6	7.95	7.62	7.23	12.7	12.2	15.8	16.1
Kincaid	69.0	71.8	68.0	67.1	68.2	63.5	7.88	7.37	7.09	12.7	11.8	15.5	14.9

Equation:

A) Char yield[1] = 32.1310 + 0.7815 (F.C.) - 0.2318 (O_2)
1) Char yield[2] = 35.7 - 0.0197 (T, °C) + 0.747 (F.C.)
2) Char yield[2] = 59.8 - 0.0192 (T, °C) + 0.583 (F.C.) - 3.26 (H_2)
3) Char yield[2] = 94.4 - 0.0951 (T, °C) + 0.000050 $(T, °C)^2$ + 0.530 (F.C.) - 4.31 (H_2)
B) Char yield[3] = 88 - 0.79 (V.M.)
C) Tar + light oil[1] = -20.8954 + 0.00333 (Btu) - 0.4624 (F.C.) ± 2.6836 (H_2)
4) Tar + light oil[2] = 26.9 - 0.0320 (T, °C) + 0.000019 $(T, °C)^2$ + 0.000688 (Btu - 11,700) - 0.0389 $(C/H_2)^2$
D) Gas yield[1] = 53.9549 - 0.00340 (Btu)
5) Gas yield[2] = 7.64 + 0.0254 (T, °C) + 0.00145 (Btu) - 0.405 (F.C.)
6) Gas yield[2] = 1.59 + 0.0393 (T, °C) - 0.000012 $(T, °C)^2$ - 0.383 (F.C.) + 0.956 (O_2)

[1] m.a.f. weight percent yields from prediction equations from RI 5904, page 37.

[2] m.a.f. weight percent yields from prediction equations listed in table 11, Appendix D.

[3] m.a.f. weight percent yields from prediction equation of Rodriguez (29).

1, 2, A (23), and B of table 4. Calculated values for char yields from equations 1 and 2 are plotted against experimental data in figures 7 and 8, respectively. Equation 3 gave the best agreement with the experimental data of any of the equations used, both at 500° C and up to and including 1,000° C, with a standard deviation of 1.50 weight percent char on an m.a.f. basis. Equation 3 is recommended for predicting char yields for North Central Province lignites.

Rodriguez's simple prediction equation, equation B (30), gave poor agreement with the experimental data at 500° C, but better agreement at higher temperatures. Since his work was done on high volatile coals using a battery of industrial coke ovens, this is to be expected. Rodriguez's equation gave a maximum deviation of plus 13 percent of the char yield, as compared with the experimental data at all temperatures.

The equation of best fit obtained for predicting yields of tar plus light oil, weight percent, m.a.f. (Y_5) was:

$$\text{Equation 4:} \quad Y_5 = 26.9 - 0.0320\,(T, °C) + 0.000019\,(T, °C)^2 + 0.000688\,(\text{Btu} - 11{,}700) - 0.0389\,(C/H_2)^2$$

A comparison of experimental data at 500° C with values calculated from the above equation and equation C (24) are also listed in table 4.

$$\text{Equation C:} \quad Y_5 = -20.8954 + 0.00333\,(\text{Btu}) - 0.4624\,(\text{F.C.}) + 2.6836\,(H_2)$$

Both of these equations gave calculated tar plus light oil values with approximately the same deviation from experimental data and were in close agreement with all but one of the experimental values. Either equation 4 or C above should be satisfactory for predicting carbonization yields of tar plus light oil at 500° C. Equation 4 gave values in closer agreement with experimental data at 500° C than at higher temperatures; but as the standard deviation was only 1.03 weight percent of tar plus light oil, reasonably close predictions of yields should be obtained. In figure 10, values calculated from equation 4 were plotted against experimental data for 500° to 1,000° C.

The product gas yield (Y_6) equation of best fit on a weight percent, m.a.f. basis was:

$$\text{Equation 6:}\quad Y_6 = 1.59 + 0.0393\,(T, {}^\circ C) - 0.000012\,(T, {}^\circ C)^2 - 0.383\,(F.C.) + 0.956\,(O_2)$$

Following is the comparable prediction equation D from table 4:

$$\text{Equation D (25):}\quad Y_6 = 53.9549 - 0.00340\,(Btu)$$

A comparison of experimental data for product gas yields at 500° C with values calculated from equations D, 6, and 5 are shown in table 4. Equation 5 gave better agreement with experimental data at 500° C than the two equations shown above, but equation 6 was preferred for carbonization temperatures of 625° to 1,000° C (see figures 11 and 12), and should be the best equation for predicting product gas yields from North Central Province lignites for the range of temperatures investigated.

The equation of best fit for heating value of product gas in Btu's on an oxygen- and nitrogen-free basis (Y_8) was:

$$Y_8 = 987 + 2.31\,(T, {}^\circ C) + 0.000477\,(T, {}^\circ C)^2 - 0.000005\,(Btu - 11{,}700)^2 - 82.2\,(C/H_2)$$

Values calculated from this equation were plotted against experimental data in figure 13. The standard deviation for this equation was 226 Btu, compared to 224 Btu for the equation plotted in figure 14. Since the above prediction equation is a function of temperature, heating value of the charge, and the carbon to hydrogen ratio of the charge, it is preferred to the equation of figure 14 involving two additional factors, oxygen and sulfur content of charge. The slightly better overall agreement with the present set of experimental data with a gas heating value standard deviation of 224 Btu does not justify the addition of two more independent variables.

Causes of Variations

Significance of char carry-over

In an attempt to determine if char carry-over into the tar-water trap was the principle factor which made the weight of charge significant, all eight single yield factors were separately tested by means of the "t" test for significant differences. Differences between yield factors from duplicate tests were separated into two sets. One set included differences for tests where char filtered from the tar-water trap was 0.5 percent or more of the initial charge weight; the other set included differences for tests where the char carry-over was less than 0.5 percent of the initial lignite charge. A test for significant difference between means at the 95 percent confidence level was made (35). Weight percent of product gas was the only yield factor significantly affected by char carry-over to the tar-water trap. Consequently, this indicated that char carry-over was not the entire reason for significance of charge weight. However, an additional unweighed amount of char (up to several grams per test) collected in the retort offtake tubes, even for some tests where less than 0.5 gram of charge was found in the tar-water trap. Other design factors may also have been contributing causes, and if changes indicated under "Recommendations" are followed, the variability of yields caused by charge weight should be reduced.

Moisture content of charge did not significantly affect the char carry-over. In fact, the average xylene moisture content of charge for tests where 0.5 percent or more of charge weight was found in the tar-water trap was lower than for tests where less than 0.5 percent of the charge weight was carried over.

Char and tar

At all conditions, some tar condensed inside of the two retort offtake tubes. For tests in which little or no uncarbonized lignite or char was carried from the retort, the quantity of tar collected in the offtake tubes was low, as shown by the closer agreement between tar yields for the 500° C tests, compared to tar yields from tests at higher temperature levels. For tests where the weight of char carry-over to the tar-water trap was measured, char carry-over was very small for all of the 500° C tests, when compared with some of the tests made at higher temperatures. A maximum weight of 0.2 gram of char was vacuum filtered from the tar-water trap from tests at 500° C, compared to 11.3 grams maximum obtained at higher temperatures.

Because the char carried out of the retort before the maximum carbonization temperature was reached was not completely carbonized, the yields were somewhat reduced. Operational and design features of the equipment made it impractical to try to obtain accurate weights on the char and tar in the gas offtake tubes, although it was determined that the quantity varied from a trace to several grams per test. Carry-over would affect all yield components to some extent.

Tar mist

For some lignites at higher temperatures, tar mist was carried into the absorption train beyond the H_2S trap. Since tar mist condensed out in the number two tar-mist trap immersed in ice water, (0.1 gram or less), it is also probable that a lesser quantity of tar mist condensed out beyond this trap (18). This tar mist could not have had a significant effect on any product yield factors, excepting H_2S and light oil. Up to 1.0 gram of water plus tar mist was condensed in the number two tar-mist trap per run.

Product gas

A number of factors contributed to variations in product gas yield and composition. These included dissolving of product gases, especially carbon dioxide, in aqueous confining solutions in the gasholders and analyzer; gas leaks, especially through sampling cock valves on gasholders; and addition of bottled nitrogen to the evacuated stainless steel storage bottle. Nitrogen addition was necessary for tests where the total volume of gas produced was between 33 and 37 liters; the latter was the minimum required for proper gas mixing using the evacuated gas sample bottle. Care was taken to minimize these factors as much as possible, but they did contribute some imprecision to the tests.

Absorption of carbon dioxide by the acidified salt brine confining solution from the product gas being analyzed would affect the methane and ethane determinations, and cause some differences in specific gravity, heating value of gas, and weight of gas yield. This gas absorption phenomenon was indicated when duplicate gas samples from each of several tests analyzed on a unit with mercury as the confining liquid, gave consistently higher ethane and lower methane results than the analyzer using the aqueous confining solution. This difference was eventually reduced by minimizing the contact time between the gas being analyzed, when it contained carbon dioxide, and the aqueous confining solution. Carbon monoxide was determined by absorption, first in acid cuprous chloride and then in cosorbent (2). This procedure circumvented absorption by the aqueous confining solution of the gas analyzer of some of the carbon monoxide, after conversion to carbon dioxide in the heated copper oxide tube.

The quantity of nitrogen added to the product gas from certain tests was determined by pressure difference, as measured on a 30 inch "U" tube manometer filled with mercury, and was calculated from the perfect gas law. It is doubtful that nitrogen addition caused significant errors, as the measured gas volume to the evacuated bottle did not vary more than ±100 ml. After it was discovered that some of the cock-type sampling valves on the gasholder leaked, short pieces of rubber tubing with pinch clamps were attached.

Carbonization product gases varied considerably in composition with temperature. Generally, carbonization at temperatures of 500° to 600° C produced higher quantities of carbon dioxide, methane, and ethane, while higher temperatures gave greater amounts of carbon monoxide and hydrogen. Thermal decomposition of the macromolecules of the coal substance results in the formation of carbon dioxide and hydrocarbons at lower temperatures, and in increased amounts of carbon monoxide and hydrogen at higher temperatures. In addition, there is the possibility of some of the gases reacting with one another or with the carbon in the lignite.

Following are some of the gas reactions that may occur:

1 $C + H_2O = H_2 + CO$

2 $C + 2H_2O = 2H_2 + CO_2$

3 $CO + H_2O = H_2 + CO_2$

4 $C + CO_2 = 2CO$

5 $C + 2H_2 = CH_4$

6 $CO + 3H_2 = CH_4 + H_2O$

7 $CO_2 + 4H_2 = CH_4 + 2H_2O$

8 $2C + 2H_2O = CH_4 + CO_2$

Equations 1 and 2 proceed only from left to right at all carbonization temperatures, with reaction 2 predominating at lower temperatures and reaction 1 at higher temperatures. Reaction 3 is believed to be insignificant at all carbonization temperatures used. Reaction 4 follows reactions 1 and 2, but is insignificant below 900° C. Therefore, a steady increase in CO and reduction in CO_2 with increasing carbonization temperatures, indicate an increasing predominance of reaction 1 over reaction 2 (5). The amount of undecomposed steam present in the retort at any time has an effect on the relative amounts of each product gas component (3).

Although the temperature at the middle of the charge did not exceed 150° C until essentially all of the free water was driven off, the external retort temperature rose to 500° C. Water of decomposition of the lignite, which averaged about 10 percent of the charge weight, was also available for the water-gas reactions at higher temperatures. With a minimum retort void volume of 184 milliliters (mls.), and a maximum gas production rate of approximately 800 mls. per minute, the minimum gas residence time in the retort was approximately 15 seconds. According to studies of the rates of formation of CO and CO_2 over charcoal for various residence times, the following table lists the amounts of CO formed at residence times approximately equal to or greater than 15 seconds.

TABLE 5

TEMPERATURE-FORMATION RATE OF CARBON MONOXIDE

Temperature, °C	Residence time, secs.	Percent by volume, CO
800	15.3	28.3
800	24.2	37.5
850	13.2	52.6
850	24.4	57.2
900	10.0	70.8
900	44.2	86.7
925	12.4	84.8
925	81.2	93.3
1,000	8.2	90.3
1,000	18.6	94.3

This table shows the increased rate of carbon monoxide formation with increasing temperature, and indicates the magnitude of carbon monoxide increase with contact time (4).

Other causes of variations in yields

Other factors that had some effect upon product yield components are:

a. Variations in heating rate and maximum temperatures reached caused by manual control and fluctuations in power line loads.

b. Increased oxidation of retorts and steel heat sink with succeeding tests caused flaking off of metal scale from both the retorts and the heat sink, particularly at higher temperatures.

c. Variations in oxidation of lignites from time of mining until carbonization.

Recommendations

Following are recommendations that should give more consistent yields from USBM assay carbonizer tests:

1. Reduction of coal charge particle size using a double-roll mill, to reduce the fines and provide a closer size consist of charge.

2. Addition of a heating element to both gas offtake tubes, to minimize condensation of tar before the tar trap.

3. Location of the furnace external and internal thermocouples at the same vertical level.

4. Development of a product-gas collection system for collecting gas in evacuated bottles, rather than over an aqueous brine solution.

5. Use of a gas analyzer with mercury as the confining liquid.

6. Replacement of the manual heat-input controller with an automatic controller, to provide for a constantly maintained heating rate instead of relying on an average heating rate.

7. Any future series of assay carbonization tests, that include tests at 500° C and higher to obtain yield data at different temperatures, should all be made using only the high temperature furnace. This would eliminate a dual furnace effect on carbonization yields observed by Goodman and associates (15).

SUMMARY AND CONCLUSIONS

Results of an analysis of variance for the four design factors showed that the mine factor was highly significant (significant at the 99 percent confidence interval) for all nine yield factors studied. Temperature was highly significant for all yield factors excepting water of formation. Weight of charge was significant at the 99 percent confidence interval for four factors and at the 95 percent interval for three factors. Moisture content of charge was only significant for light oil and hydrogen sulfide. Replicates were not significant at the 95 percent confidence interval. Yields of char, tar plus light oil, and product gas were essentially linear functions of temperatures at 625° C and higher. Heating value of product gas (Btu per pound of lignite charged, m.a.f.) was a linear function at or above 750° C. (See figures 3 through 6).

Prediction equations were developed for yields of char, tar, light oil, tar plus light oil, product gas, and heating value of product gas. Some function of temperature and one or more factors of the proximate and/or ultimate analyses of the lignite charges were the independent variables. Accepted equations gave multiple correlation coefficients of from 0.876 to 0.976. Several prediction equations were selected as the most suitable for predicting yields of char, tar plus light oil, product gas, and heating value of product gas. Calculated values from the best prediction equations developed in this work were in closer agreement with the experimental data for char, tar plus light oil, and product gas yield at 500° C than values calculated from equations developed by other researchers. Recommended equations for predicting yields of char, tar plus light oil, and product gas, respectively, on an m.a.f. weight percent basis are:

$$\text{Char yield} = 94.4 - 0.0951\,(T,\ ^\circ C) + 0.000050\,(T,\ ^\circ C)^2 + 0.530\,(F.C.) - 4.31\,(H_2)$$

$$\text{Tar plus light oil yield} = 26.9 - 0.0320\,(T,\ ^\circ C) + 0.000019\,(T,\ ^\circ C)^2 + 0.000688\,(\text{Btu} - 11{,}700) - 0.0389\,(C/H_2)^2$$

$$\text{Product gas yield} = 1.59 + 0.0393\,(T,\ ^\circ C) - 0.000012\,(T,\ ^\circ C)^2 - 0.383\,(F.C.) + 0.956\,(O_2)$$

Due to the significant influence of weight of charge, it is recommended that this factor be specified at some level for future tests with the USBM assay carbonizer. Also, only the high-temperature furnace should be used for any future series of tests for statistical analysis of the data.

APPENDIX A

IDENTIFICATION OF SYMBOLS AND ABBREVIATIONS

Btu - British thermal units.
C - Carbon.
CH_4 - Methane.
C_2H_6 - Ethane.
CO - Carbon monoxide.
CO_2 - Carbon dioxide.
Cu ft - Cubic feet.
DF - Degrees of freedom.
Fc - Critical F value at level specified.
FC - Fixed carbon.
H, H_2 - Hydrogen.
H_2S - Hydrogen sulfide.
H_2O - Water.
i - Columns in statistical design.
ID - Inside diameter.
Ill. - Illuminants in product gas.
j. - Rows in statistical design.
k - Replicates.
LO - Light oil.
M - Montana.
mls. - Milliliters.
m.a.f. - Moisture and ash free.

APPENDIX A Continued

IDENTIFICATION OF SYMBOLS AND ABBREVIATIONS

m.f. - Moisture free.

MS - Mean square.

N, N_2 - Nitrogen.

O, O_2 - Oxygen.

OD - Outside diameter.

Rc - Critical correlation coefficient at level specified.

Rm - Multiple correlation coefficient.

S - Sulfur.

Sav. - Savage mine (Montana).

SS - Sum of squares.

s.s. - Stainless steel.

T - Temperature, °C.

USBM - United States Bureau of Mines.

VM - Volatile matter.

Wt. % - Weight percent.

X - Independent variable.

X_i - Column effect.

X_j - Row effect.

X_k - Replicates effect.

X_{ijk} - Refers to each of 50 data points for analysis of variance.

Y - Dependent variable.

Y_1 - Char yield.

Y_2 - Water of formation yield.

APPENDIX A Continued

IDENTIFICATION OF SYMBOLS AND ABBREVIATIONS

Y_3 - Tar yield.

Y_4 - Light oil yield.

Y_5 - Tar plus light oil yield.

Y_6 - Product gas yield.

Y_7 - Hydrogen sulfide yield.

Y_8 - Heating value of product gas (O_2-N_2 free), Btu/lb coal, m.a.f.

α - 15 percent xylene moisture in lignite charge.

β - 20 percent xylene moisture in lignite charge.

γ - 25 percent xylene moisture in lignite charge.

λ - 30 percent xylene moisture in lignite charge.

ε - 35 percent xylene moisture in lignite charge.

σ^2 - Variance.

σ_α^2 - Variance for mines.

σ_β^2 - Variance for temperature levels.

σ_γ^2 - Variance for moisture content of charge levels.

σ_λ^2 - Variance for weight of charge levels.

σ_ε^2 - Variance for the error term.

σrep^2 - Variance for replicates.

APPENDIX B

EQUIPMENT AND INSTRUMENTS

Equipment

Electrically heated low-temperature furnace, 500° C.

Electrically heated high-temperature furnace, 1,000° C.

Powerstat, 0-100 volts, 45 amps, 6.1 KVA.

Gasholders, 2, 16.5 liters capacity each, 4 inches OD x 9-1/2 feet long, s.s.

Gasholder, vacuum, 34.1 liters capacity, s.s.

Retorts, 1-7/8 inches ID x 7 inches, low carbon steel, 500° C.

Retort, 1-7/8 inches ID x 8 inches, s.s., 625 to 1,000° C.

Reservoirs, salt-brine, 6 inches ID x 62 inches, s.s.

Product gas recycle pump, 120 rpm; Chevrolet pickup fuel pump.

Gear reducer, 10 to 1 ratio, with 1/4 hp motor, 1725 rpm.

Dean-Stark xylene distillation apparatus.

Analytic balance, Ainsworth chainomatic, 200 grams capacity.

Double pan scale, Fisher, calibrated to 0.1 gram, 2000 grams capacity.

Drying oven for coal samples, electrically heated.

Swinghammer crusher, Grundler type.

Instruments

One Brown Electronik four point temperature recorder, 0 to 1,000° C.

One Brown Electronik four point temperature recorder, 0 to 2,400° F.

Two chromel-alumel thermocouples, 22 gage wire, external.

Two chromel-alumel thermocouples, 22 gage wire, with 1/4 inch OD s.s. wells.

One chromel-alumel thermocouple, 22 gage wire, 3/16 inch OD s.s. wells.

APPENDIX B Continued

Instruments

Four dial type bimetallic thermometers, Weston, 0 to 220° F, 2° F divisions.

Gas analyzer, Orsat type, buildup model.

Gas analyzer, Burrell, buildup model No. 38-772, H_g confining liquid.

Manometers, U tube, water, 25 inches.

Manometer, U. tube, mercury, 15 inches.

CA-24	CA-25	CA-28	CA-30	CA-31	CA-33	CA-34	CA-35	CA-38
Sav., M.	Kincaid	Kincaid	Velva	Velva	Sav., M.	Velva	Beulah	Kincaid
875	875	750	500	875	1,000	1,000	1,000	1,000
19.8	25.1	20.1	18.7	34.8	25.2	15.1	35.8	30.9
159.7	119.6	149.8	128.4	140.3	130.4	160.2	150.6	140.1
9.18	9.42	10.58	6.73	4.97	8.83	6.25	6.64	9.17
63.7	58.3	58.9	67.3	58.2	60.6	58.9	56.4	57.5
8.0	10.2	11.0	10.3	9.3	8.0	10.4	10.0	9.9
2.2	5.6	6.2	5.5	7.0	1.9	3.7	5.1	6.2
0.9	1.1	1.0	0.9	1.1	1.0	1.0	1.0	1.2
23.3	24.0	22.0	15.5	24.9	27.4	24.7	26.8	24.6
0.3	0.2	0.2	0.3	0.1	0.3	0.1	0.4	0.1
98.4	99.4	99.3	99.8	100.6	99.2	98.8	99.7	99.5
21.6	19.2	19.1	46.8	20.5	20.8	18.6	17.0	16.1
0.4	0.4	0.4	0.6	0.3	0.4	0.2	0.4	0.5
19.0	15.3	15.6	13.4	17.1	18.6	16.3	17.9	14.8
39.6	46.7	43.4	12.5	43.0	41.6	44.5	45.8	49.3
18.6	17.1	20.9	25.1	18.3	18.6	20.4	18.9	19.2
0.8	1.3	0.6	1.6	0.8	0.0	0.0	0.0	0.1
4.640	5.359	4.812	2.006	5.243	5.650	5.486	6.120	6.007
1,863	2,185	2,041	765	2,100	2,227	2,241	2,492	2,492
401.6	407.7	424.1	381.2	400.5	394.1	408.5	407.2	414.8
0.655	0.585	0.597	1.011	0.619	0.632	0.587	0.573	0.535
45.25	44.29	45.02	45.73	44.98	45.86	44.44	45.29	43.93
54.75	55.71	54.98	54.27	55.02	54.14	55.56	54.71	56.07
4.56	4.84	4.85	4.72	4.72	4.52	4.66	4.75	4.93
73.12	73.07	73.09	71.87	72.53	73.17	72.64	73.34	73.64
1.19	1.22	1.19	1.12	1.19	1.13	1.14	1.03	1.22
19.88	20.22	20.13	21.80	21.19	20.01	21.14	19.21	19.57
1.25	.65	0.74	0.49	0.37	1.17	0.42	1.67	0.64
11,880	12,230	12,150	11,870	12,040	11,950	12,140	12,210	12,450
2.92	3.52	3.45	15.33	6.00	5.26	4.22	3.19	4.19
78.14	76.13	76.09	73.42	80.22	74.49	80.21	79.99	76.00
18.94	20.35	20.46	11.25	13.78	20.25	15.57	16.82	19.81
12,304	11,910	11,870	12,860	12,905	12,250	12,640	12,710	11,850

CA-50	CA-53	CA-54	CA-56	CA-57	CA-58	CA-59	CA-60	CA-61
Beulah	Beulah	Beulah	Sav., M.	Sav., M.	Peerless	Beulah	Kincaid	Velva
875	500	750	500	625	625	625	1,000	1,000
30.7	15.3	25.9	29.1	35.1	29.7	20.2	30.3	14.2
130.5	119.7	160.3	150.7	120.2	160.1	120.6	140.0	160.2
7.43	8.75	7.45	7.80	7.65	10.78	8.73	9.00	6.14
58.4	67.5	62.4	69.0	64.6	62.5	63.0	55.4	60.2
9.8	10.2	9.5	10.3	8.8	10.4	11.3	11.0	9.1
3.4	6.7	3.6	4.5	2.3	4.2	3.3	6.0	3.7
1.2	0.9	0.9	0.9	1.1	1.2	1.0	1.1	0.9
27.8	14.1	22.9	15.2	22.8	20.5	21.2	25.6	25.1
0.4	0.9	0.5	0.4	0.2	0.8	0.6	0.4	0.2
101.0	100.3	99.8	100.3	99.8	99.6	100.4	99.5	99.2
22.6	48.5	21.7	54.2	33.9	30.3	30.8	16.6	19.1
0.5	0.9	0.5	0.7	0.3	0.5	0.6	0.5	0.4
15.4	12.4	18.3	11.9	16.2	16.8	15.9	16.5	17.0
40.6	10.4	39.7	9.2	28.0	27.2	26.8	47.6	45.5
20.4	25.8	16.7	20.8	19.7	22.2	25.1	18.7	17.4
0.5	2.0	3.1	3.2	1.9	3.0	0.8	0.1	0.6
5.627	1.768	4.275	1.807	3.714	3.419	3.486	6.034	5.514
2,300	692	1,812	636	1,427	1,480	1,469	2,473	2,202
408.7	391.4	423.9	352.1	384.1	432.9	421.3	409.8	399.4
0.645	1.043	0.665	1.103	0.803	0.782	0.794	0.555	0.594
45.34	45.46	45.51	45.02	43.70	48.45	46.10	44.67	43.57
54.66	54.54	54.49	54.98	56.30	51.55	53.90	55.33	56.43
4.69	4.66	4.61	4.65	4.34	4.46	4.30	5.30	4.89
73.12	73.47	72.94	72.93	73.21	72.57	73.35	73.17	73.18
0.97	0.94	0.96	1.12	1.13	0.99	0.95	1.09	1.14
19.48	19.39	19.88	20.07	20.25	20.49	19.66	19.61	20.41
1.74	1.54	1.61	1.23	1.07	1.49	1.74	0.83	0.38
12,240	12,320	12,170	12,050	11,900	12,170	12,260	12,300	12,250
5.06	18.71	6.13	17.95	10.12	10.78	9.27	1.54	4.86
78.65	67.72	78.14	67.56	74.08	66.35	74.67	76.04	80.65
16.29	13.57	15.73	14.49	15.80	22.87	16.06	22.42	14.49
12,760	12,690	12,750	12,330	12,680	11,720	13,070	11,680	12,820

CA-67	CA-68	CA-69	CA-70	CA-71	CA-72	CA-73	CA-74	CA-75
Sav., M.	Peerless	Beulah	Peerless	Velva	Kincaid	Velva	Peerless	Peerless
750	500	625	625	750	625	625	750	875
14.4	25.5	20.2	29.7	30.0	15.4	24.6	35.0	15.8
140.2	139.8	139.7	160.1	120.1	130.1	149.7	129.8	150.6
10.34	11.56	8.11	10.51	6.14	10.84	6.02	9.53	12.67
61.3	68.3	62.4	60.0	58.5	62.9	62.8	56.4	55.7
9.3	9.3	10.6	11.2	9.7	10.4	10.7	10.5	10.8
2.5	3.9	5.0	4.6	4.3	5.3	3.6	3.8	4.9
0.9	1.0	0.9	1.1	1.1	1.0	1.0	1.4	1.1
25.5	17.1	20.7	22.7	26.1	20.6	22.0	27.7	26.7
0.3	0.8	0.5	0.8	0.3	0.2	0.1	0.4	0.8
99.8	100.4	100.1	100.4	100.0	100.4	100.2	100.2	100.0
24.2	50.1	29.6	33.2	22.0	28.5	32.2	24.1	20.7
0.5	0.9	0.7	0.9	0.7	0.8	0.8	0.9	0.8
19.5	11.2	16.0	16.2	18.1	14.2	15.5	18.2	18.7
36.1	9.9	28.3	24.0	39.1	31.7	27.8	36.8	39.4
18.7	24.5	23.4	23.2	19.0	22.4	21.4	18.0	18.2
1.0	3.4	2.0	2.5	1.1	2.4	2.3	2.0	2.2
4.734	2.100	3.460	3.522	5.151	3.494	3.536	5.159	5.318
1,883	836	1,493	1,516	2,126	1,524	1,472	2,152	2,290
397.8	397.9	431.4	430.5	412.8	436.2	416.4	417.1	430.6
0.703	1.059	0.782	0.844	0.662	0.769	0.813	0.701	0.656
44.80	49.16	45.94	45.03	44.27	43.82	44.76	48.36	48.90
55.20	50.84	54.06	54.97	55.73	56.18	55.24	51.64	51.10
4.58	4.98	4.83	5.22	4.69	4.86	4.70	4.98	5.05
73.64	72.49	72.56	76.38	72.33	72.52	71.73	71.40	71.90
1.12	0.98	0.91	1.13	1.08	1.12	1.08	0.97	0.95
19.41	20.07	20.02	15.98	21.13	20.88	22.11	21.34	20.58
1.25	1.51	1.68	1.29	0.57	0.62	0.38	1.31	1.52
12,020	12,110	12,180	12,980	11,970	12,240	11,810	11,940	12,050
6.17	7.06	8.71	9.34	6.60	10.39	8.90	7.20	6.51
75.96	72.48	75.63	67.03	79.63	71.01	78.52	70.85	67.21
17.87	20.46	15.66	23.63	13.77	18.60	12.58	21.95	26.28
12,406	11,630	13,010	11,680	12,950	12,280	12,970	11,811	11,218

CA-81 Peerless	CA-82 Velva	CA-83 Sav., M.
500	625	500
25.5	24.1	28.7
139.7	149.9	150.4
11.13	6.68	7.47
65.5	62.1	68.9
9.4	11.0	10.4
7.1	3.4	5.1
1.0	1.0	0.8
16.3	22.5	14.8
0.8	0.1	0.4
100.1	100.1	100.4
50.6	32.1	55.0
1.3	0.8	1.3
12.7	16.3	12.6
9.6	27.3	8.2
22.7	21.6	20.3
3.1	1.9	2.6
1.976	3.618	1.723
765	1,489	601
386.9	411.6	349.0
0.750	0.812	1.122
48.52	46.03	44.82
51.48	53.97	55.18
4.93	4.65	4.57
71.54	70.99	72.02
0.80	1.02	1.10
21.38	22.77	21.45
1.35	0.57	0.86
12,010	11,780	11,800
14.73	11.08	23.53
64.48	76.09	61.11
20.79	12.83	15.32
11,520	12,900	12,550

APPENDIX D

TABLE 1

ANALYSIS OF VARIANCE FOR CHAR YIELD (Y_1), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	130.6372	4	32.6593	30.025[1]
Temperatures	691.9772	4	172.9943	159.042[1]
Moistures in charges	4.3452	4	1.0863	0.999
Weights of charges	30.2212	4	7.5553	6.946[1]
Replicates	2.1632	1	2.1632	1.989
Error	34.8072	32	1.0877	---
Total	894.1512	49	---	---

[1] Significant at the 99 percent confidence interval.

TABLE 2

ANALYSIS OF VARIANCE FOR WATER OF FORMATION (Y_2), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	16.102	4	4.0255	9.434[1]
Temperatures	3.726	4	0.9315	2.183
Moistures in charges	3.500	4	0.8750	2.051
Weights of charges	4.186	4	1.0465	2.453
Replicates	0.0392	1	0.0392	0.092
Error	14.007	32	0.4267	---
Total	41.5602	49	---	---

[1] Significant at the 99 percent confidence interval.

APPENDIX D Continued

TABLE 3

ANALYSIS OF VARIANCE FOR DRY TAR YIELD (Y_3), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	50.1868	4	12.5467	26.718[1]
Temperatures	20.5288	4	5.1322	10.929[1]
Moistures in charges	4.6308	4	1.1577	2.465
Weights of charges	8.1468	4	2.0367	4.337[1]
Replicates	0.5618	1	0.5618	1.196
Error	15.0268	32	0.4696	---
Total	99.0818	49	---	---

[1] Significant at the 99 percent confidence interval.

TABLE 4

ANALYSIS OF VARIANCE FOR LIGHT OIL YIELD (Y_4), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	0.32218	4	0.080545	16.215[1]
Temperatures	0.10064	4	0.025160	5.065[1]
Moistures in charges	0.16166	4	0.040415	8.136[1]
Weights of charges	0.12072	4	0.030180	6.076[1]
Replicates	0.00205	1	0.00205	0.413
Error	0.15895	32	0.004967	---
Total	0.86620	49	---	---

[1] Significant at the 99 percent confidence interval.

APPENDIX D Continued

TABLE 5

ANALYSIS OF VARIANCE FOR DRY TAR PLUS LIGHT OIL YIELD (Y_5), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	56.020	4	14.0050	30.196[1]
Temperatures	17.104	4	4.2760	9.219[1]
Moistures in charges	4.366	4	1.0915	2.353
Weights of charges	8.386	4	2.0965	4.520[1]
Replicates	0.4232	1	0.4232	0.912
Error	14.8408	32	0.4638	---
Total	101.1400	49	---	---

[1] Significant at the 99 percent confidence interval.

TABLE 6

ANALYSIS OF VARIANCE FOR O_2 AND H_2 FREE PRODUCT GAS YIELD (Y_6), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	54.2048	4	13.5512	21.137[1]
Temperatures	889.7228	4	222.4307	346.952[1]
Moistures in charges	6.2548	4	1.5637	2.439
Weights of charges	25.8568	4	6.4642	10.083[1]
Replicates	0.1800	1	0.1800	0.281
Error	20.5136	32	0.6411	---
Total	996.7328	49	---	---

[1] Significant at the 99 percent confidence interval.

APPENDIX D Continued

TABLE 7

ANALYSIS OF VARIANCE FOR HYDROGEN SULFIDE YIELD (Y_7), M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	1.570992	4	0.392748	49.474[1]
Temperatures	0.420232	4	0.105058	13.234[1]
Moistures in charges	0.137812	4	0.034453	4.340[1]
Weights of charges	0.107812	4	0.026953	3.395[2]
Replicates	0.001152	1	0.001152	0.145
Error	0.254032	32	0.007939	---
Total	2.492032	49	---	---

1/ Significant at the 99 percent confidence interval.

2/ Significant at the 95 percent confidence interval.

TABLE 8

ANALYSIS OF VARIANCE FOR HEATING VALUE OF PRODUCT GAS (Y_8), (O_2 AND N_2 FREE BASIS), BTU/LB OF COAL, M.A.F. BASIS

Source	Sum of squares	DF	Mean square	F
Mines	405,233.1	4	101,308.275	6.206[1]
Temperatures	64,864,956.4	4	16,216,239.1	99.334[1]
Moistures in charges	51,528.9	4	12,882.225	0.789
Weights of charges	182,837.9	4	45,709.475	2.800[2]
Replicates	17,974.1	1	17,974.1	1.101
Error	522,399.1	32	16,324.972	---
Total	66,044,929.5	49	---	---

1/ Significant at the 99 percent confidence interval.

2/ Significant at the 95 percent confidence interval.

APPENDIX D Continued

TABLE 9

ANALYSIS OF VARIANCE FOR HEATING VALUE OF PRODUCT GAS (O_2 AND N_2 FREE BASIS), BTU/STD. CU. FT.

Source	Sum of squares	DF	Mean square	F
Mines	9,260.08	4	2,315.02	27.950[1]
Temperatures	5,862.28	4	1,465.57	17.694[1]
Moistures in charges	257.48	4	64.37	0.777
Weights of charges	801.28	4	200.32	2.419
Replicates	0.18	1	0.18	0.002
Error	2,650.48	32	82.83	---
Total	18,831.78	49	---	---

[1] Significant at the 99 percent confidence interval.

X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	σ[4]	DF[5]	Correlation coefficients Rm	 Rc
						2.03	43	0.895	0.380
						2.05	43	0.894	0.380
H_2						1.45	42	0.950	0.385
						2.19	47	0.865	0.365
						2.60	48	0.824	0.361
						2.01	46	0.890	0.368
						2.10	46	0.879	0.368
						2.10	47	0.876	0.360
						1.48	43	0.945	0.380
						1.50	45	0.942	0.372
						1.93	44	0.894	0.376
H_2	C/H_2	O_2/H_2	H_2C	S	C	0.93	37	0.980	0 408
C						0.89	42	0.979	0.385
						0.97	44	0.975	0.376
						1.35	46	0.948	0.368
						1.34	47	0.947	0.365
						2.33	48	0.826	0.361
						1.03	45	0.970	0.372
						1.33	46	0.949	0.368
						0.91	44	0.796	0.376
						1.17	43	0.984	0.380
						1.16	45	0.984	0.372
						1.42	47	0.975	0.365
O_2/H_2	C					0.92	41	0.806	0.389
						0.275	43	0.983	0.380
						0.273	46	0.982	0.368
						0.271	47	0.982	0.365
						0.818	48	0.818	0.361
						2.00	43	0.973	0.380
						2.00	45	0.972	0.372
						2.11	47	0.967	0.365
C/H_2	O_2/H_2	C.				1.94	40	0.976	0.393
						1.86	45	0.976	0.372
						2.11	46	0.968	0.368
						2.24	46	0.963	0.368

								Correlation coefficients	
X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	σ[4]	DF[5]	Rm	Rc
H_2	C/H_2	O_2/H_2	H_2O	S	C	235.	37	0.973	0.413
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	224.	43	0.971	0.380
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	225.	45	0.969	0.372
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	229.	46	0.968	0.368
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	233.	47	0.966	0.365
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	238.	48	0.964	0.361
. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	226.	45	0.969	0.372

[1] Units and definitions of independent variables in this table are:

T - Temperature of carbonization, °C.
Btu - British thermal units, m.a.f. heating value.
F.C. - Fixed carbon, m.a.f. weight percent.
O_2 - Oxygen content, m.a.f. weight percent.
H_2 - Hydrogen content, m.a.f. weight percent.
C/H_2 - Carbon to hydrogen ratio, m.a.f. weight percent.
O_2/H_2 - Oxygen to hydrogen ratio, m.a.f. weight percent.
H_2O - Xylene moisture content, weight percent.
S - Sulfur content, m.a.f. weight percent.
C - Carbon content, m.a.f. weight percent.

[2] m.a.f. weight percent.

[3] Btu in gas per pound of lignite, m.a.f.

[4] Residual standard deviation of "Y" after regression.

[5] Residual degrees of freedom used to determine the multiple correlation coefficient (Rm) and the critical correlation coefficient (Rc) at the 99 percent confidence interval.

APPENDIX D Continued

TABLE 11

PREDICTION EQUATIONS AND CONSTANTS FOR LIGNITE ASSAY CARBONIZATION

Equation	Rm	σ
(1) Char yield, weight percent, m.a.f. = 35.7 − 0.0197 (T,°C) + 0.747 (F.C.)	0.876	2.10
(2) Char yield, weight percent, m.a.f. = 59.8 − 0.0192 (T,°C) + 0.583 (F.C.) − 3.26 (H_2)	0.890	2.01
(3) Char yield, weight percent, m.a.f. = 94.4 − 0.0951 (T,°C) + 0.000050 $(T,°C)^2$ + 0.530 (F.C.) − 4.31 (H_2)	0.942	1.50
(4) Tar + light oil yield, weight percent, m.a.f. = 26.9 − 0.0320 (T,°C) + 0.000019 $(T,°C)^2$ + 0.000688 (Btu-11,700) − 0.0389 $(C/H_2)^2$	0.970	1.03
(5) Gas yield (O_2-N_2 free) weight percent, m.a.f. = 1.59 + 0.0393 (T,°C) − 0.000012 $(T,°C)^2$ − 0.383 (F.C.) + 0.956 (O_2)	0.976	1.86
(6) Gas yield (O_2-N_2 free) weight percent, m.a.f. = 7.64 + 0.025 (T,°C) − 0.00145 (Btu) − 0.405 (F.C.)	0.963	2.24
(7) Heating value of gas (O_2-N_2 free) weight percent, m.a.f. = 987 + 2.31 (T,°C) + 0.000477 $(T,°C)^2$ − 0.000005 $(Btu-11,700)^2$ − 82.2 (C/H_2)	0.969	226.
(8) Heating value of gas (O_2-N_2 free) weight percent, m.a.f. = −736 + 2.89 (T,°C) + 0.127 (Btu) − 20.1 (F.C.) + 49.3 (O_2) − 73.4 (C/H_2) + 0.393 (S)	0.971	224.

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