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Activated Carbon from North Dakota Lignite

John R. McNally

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ACTIVATED CARBON
FROM
NORTH DAKOTA LIGNITE

by

John R. McNally
Bachelor of Science,
University of North Dakota 1968

A Thesis
Submitted to the Faculty
of the
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in partial fulfillment of the requirements
for the degree of
Master of Science

Grand Forks, North Dakota

February
1970

This Thesis submitted by John R. McNally in partial fulfillment of the requirements for the degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

/s/ Wayne R. Kube
(Chairman)

/s/ Robert C. Ellman

/s/ Thomas J. Clifford

/s/ A. W. Johnson
Dean of the Graduate School

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Permission

Title Activated Carbon from North Dakota Lignite

Department Chemical Engineering

Degree Master of Science

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Date   September 12, 1969

ACKNOWLEDGEMENTS

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ABSTRACT

Activated carbon was produced by reacting lignite char with steam in a fluidized-bed reactor which was designed and constructed for this study. Effects of three variables, temperature, residence time and particle size, at four levels were studied statistically using a Latin square design. When the analysis of variance indicated that only two of the variables, temperature and residence time, were significant, a two-way classification design was used to investigate optimum activation conditions.

Activated carbon with adsorptive powers which were equal to or superior to Darco active carbon, as shown by the iodine test and the color adsorption test, were produced in this study. The best active carbons had an iodine adsorption of .725 grams per gram of carbon while Darco was only .55 grams of iodine per gram of carbon. Darco removed only 4 percent of the color from a stock solution of malachite green indicator while many of the products of this investigation removed 75 to 85 percent.

The analysis of variance of the results of the two designs used indicate that the effects of residence time between 6 minutes to 24 minutes is greater than that of temperature from 1450° F to 1750° F.

INTRODUCTION

An economical process for the production of activated carbon from lignite would be advantageous to the State of North Dakota which has abundant deposits of lignite but only a limited market. Between 1910 and 1962, the last year for which data was available, the consumption of activated carbon has risen from 10,000 to 65,000 tons per year.[1] The increased emphasis on pollution and environment control will create an even greater demand in the future. The value of 65,000 tons of activated carbon was approximately $32 million in 1962.

Heat and mass transfer characteristics indicate that a fluidized bed could be used in activating lignite with steam. Thelen[2] and Singh[3] attempted to produce activated carbon in a partially fluidized bed with some success, but they did not investigate one of the important variables, residence time. Some of their carbons compared favorably with Darco, an activated carbon made from Texas lignite by the Atlas Chemical Company, for gas adsorption, but no attempt was made to test for liquid system adsorption.

The present study is concerned with steam activation of a char derived from North Dakota lignite in a true fluidized bed with emphasis on the effects residence time, particle size, and temperature have on activity of the carbon in a liquid system. It was also desired that the equipment be viable enough that later workers could continue the study.

HISTORICAL AND GENERAL INFORMATION

In the past, adsorbent carbonaceous materials have been referred to as decolorizing carbon, bone char, blood char, coconut char, as well as by various trade names.[4] Such nomenclature came about by the association with the function the carbon performed or by the source of raw material. At the present time, any specially prepared carbonaceous material which has significant adsorptive properties is referred to as active carbon or activated carbon.

According to Hassler,[5] Scheele discovered the ability of carbon to adsorb gases in 1773, and Lowitz, in 1785, observed that charcoal would decolorize many solutions, but activated carbon was not commercially important until 1808. In that year activated carbon was used to clarify beet sugar. From 1808 until 1915 nearly all research was directed toward finding a better carbon for sugar decolorization. During World War I, the use of chlorine gas prompted research that led not only to gas masks but also to development of gas adsorbing activated carbon for research and industry.

3. Processes depending solely on heat to eliminate the hydro-carbons. This process, when carried out in the absence of air, is called carbonization.

4. Processes depending on selective oxidation to break down and remove the hydrocarbons and later to increase the porosity of the carbon.

Today, only selective oxidation and the action of metallic chlorides are used extensively, although carbonization is used to prepare material, such as lignite, for activation. Hassler[14] points out that zinc, calcium and magnesium chlorides are used primarily to improve the decolorization ability of the carbon while selective oxidation enhances the ability of the carbon to adsorb gases, color or odor, or any combination of the three depending on the combination of starting materials, pretreatment, and method of activation.

Generally, the metal chlorides are used by mixing the carbonaceous material with the salt and then wetting thoroughly with water. This mixture is then dried and carbonized at temperatures between $800°$ and $1,200°$ F. The product is then washed to remove excess salts and activated with steam or some other oxidizing gas.

In addition to the effect of starting material, the adsorptive powers of an active carbon which have been produced by oxidation are influenced by:[15]

1. The chemical nature and concentration of the oxidizing gas;

2. The temperature of the reaction;

3. The reaction time; and

4. Presence of minerals in the material.

Some of the more common oxidizing gases for activation are steam, carbon dioxide and oxygen, which are passed over, through, around or released from a compound added to the material to be activated. Steam is the most commonly used of the oxidizing gases. Active carbon has been produced from lignite and other materials by contacting it with steam using various schemes. The reactions, which are endothermic and occur at appreciable rates only at high temperatures, are:

$$C + H_2O \rightarrow H_2 + CO \qquad H = -56,400 \frac{cal}{g\ Mole}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad H = -38,750 \frac{cal}{g\ Mole}$$

3
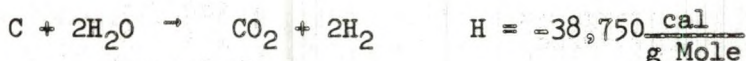
necessary to construct a device to heat the reactor. A product collection system and a charging device were necessary also. All of the temperatures were measured by chromel-alumel thermocouples and recorded by a four point Bristol recorder. A description of the various pieces of equipment follows.

Superheated Steam Generator - It was necessary to deliver steam at 1,900° F to the reactor to activate char at 1,750° F. This was accomplished using a pair of gas heated coils followed in series by an electrically-heated furnace. Steam was superheated using gas-fired burners to 900° F in the first two coils and to 1,900° F in the electric furnace. A reciprocal pump, which was calibrated and set to deliver 2.2 pounds per hour, was used to feed the steam generator, and a 10 amp powerstat was used to control the temperature. A schematic drawing of the steam heating system is shown in figure 1.

Reactor Heater - A heater which was capable of maintaining a reactor temperature of at least 1,750° F was needed. The heat requirements, which included all radiation, convection, and conduction losses as well as any heat energy used by the reaction, were estimated to be less than 4-kw. It was found that the heater, which had a power capability of 6-kw, was more than adequate. The heat was provided by passing electrical current through four silicon carbide resistance bars. These bars were contained in a well-insulated box, and two 25 amp powerstats were used to control the temperatures.

An electrical resistance wire heating system was originally used, but was abandoned after operating difficulties became apparent.

Fluidized Bed Reactor - A 30 inch section of three-inch O.D. stainless steel pipe formed the reactor body. A one-inch sintered alumina plate was imbedded in the walls of the reactor about one and one half inches above the bottom. This served to disperse the entering steam evenly over the bed to promote fluidization. There were three openings in the bottom chamber, one for the superheated steam, one for inert gas, and one for a thermocouple which was just below the alumina plate. A thermocouple extended from the top of the reactor to within one inch of the alumina plate. This thermocouple was adjustable to any desired height above the plate to make possible a temperature profile of the fluidized bed. The thermocouple was also removable, since it entered the reactor through the reactor feed port. Details are given in figure 3.

Charging Device - A method of charging 400 grams of heated char quickly and efficiently was required. The following device worked satisfactorily.
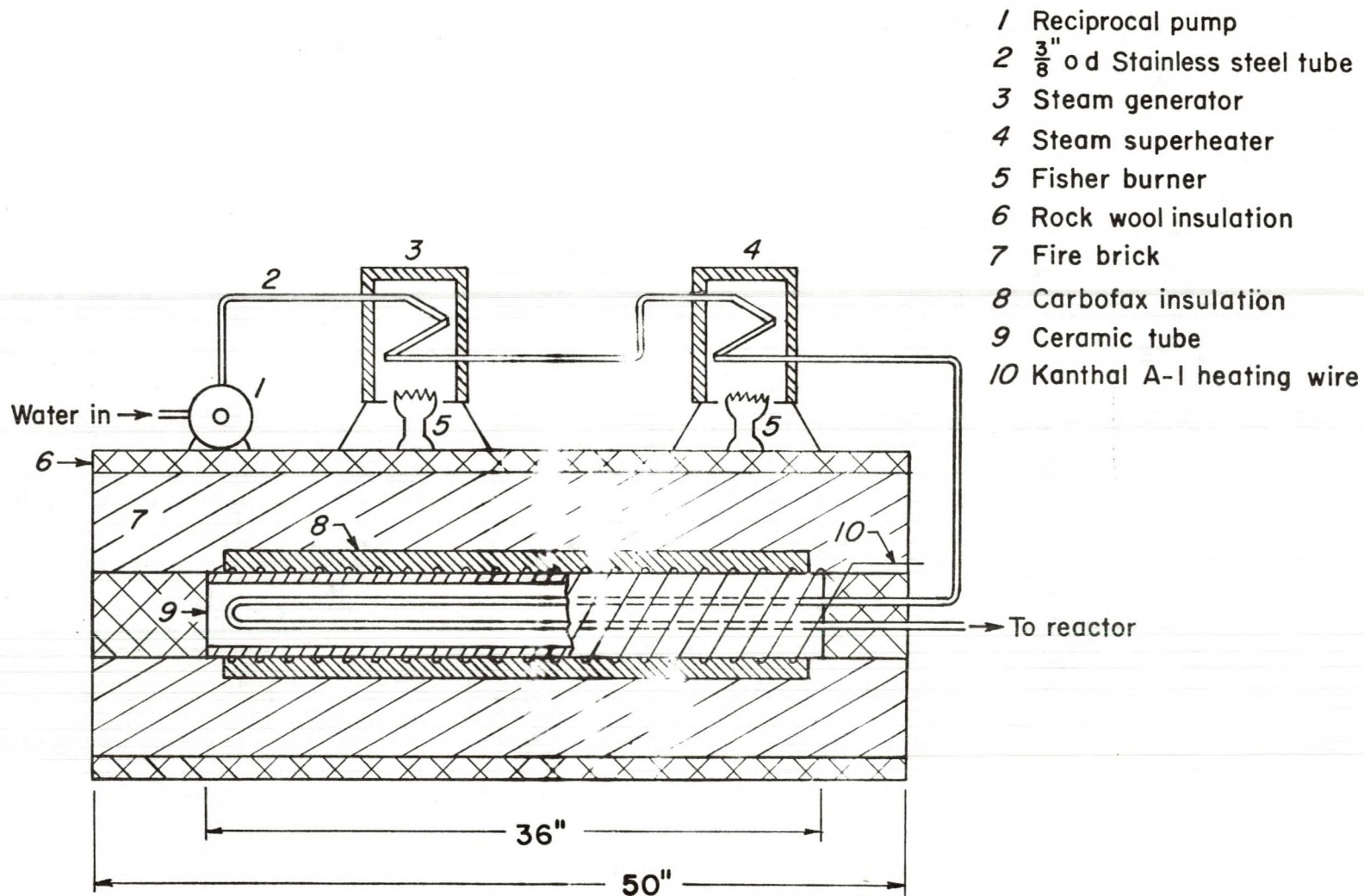
Fig 1   Details of superheated steam generator

1 Reciprocal pump
2 $\frac{3}{8}$" od Stainless steel tube
3 Steam generator
4 Steam superheater
5 Fisher burner
6 Rock wool insulation
7 Fire brick
8 Carbofax insulation
9 Ceramic tube
10 Kanthal A-1 heating wire

22" sq
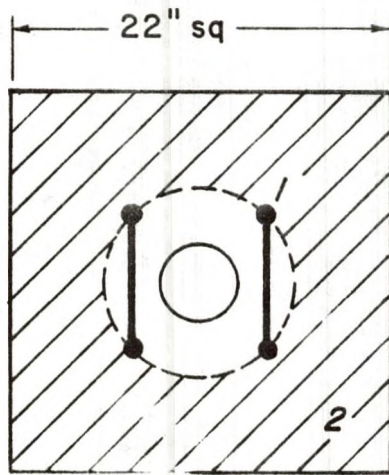
1 4 - $\frac{5}{8}$" x 41" Silicon carbide heating bars, 2 on each side connected in series.

2 Infrax brick insulation

5"

4"

23"

38"

Connected to 25 amp powerstat

Connected to 25 amp powerstat

Fig 2 Details of reactor heater.

→ To temperature recorder

To ←
cyclone

← From superheated steam
generator

1

2

31"

1 Stainless steel reactor, 3" o d
2 Stainless steel tube, $\frac{3}{8}$" o d
3 Adjustable thermocouple
4 Sintered alumina plate, 1" thick
5 Thermocouple

3

4

$\frac{1}{2}$"

5

← N_2 (pressurized)
→ To temperature recorder

Fig 3 Details of fluidized bed reactor.

A two-inch O.D. steel pipe was fitted with a cover and a nipple as shown in figure 4. A threaded bottom with a 23-inch section of three fourths inch O.C. stainless steel tube was attached. When the charger was attached to the top of the reactor and a pressurized nitrogen line attached to the nipple, 400 grams of char could be charged in about 20 seconds.

Product Collection - The product was collected from the reactor by applying nitrogen pressure in the chamber below the sintered alumina plate. A high flow of nitrogen through the reaction zone carried the product out of the reactor into a cyclone separator. The separator allowed the gases to pass to the atmosphere while the solids fell into the collection chamber. Details can be seen on figure 5.

OPERATING PROCEDURE

The steam generators and the reactor heater were started about 24 hours before the tests were to be run. The temperature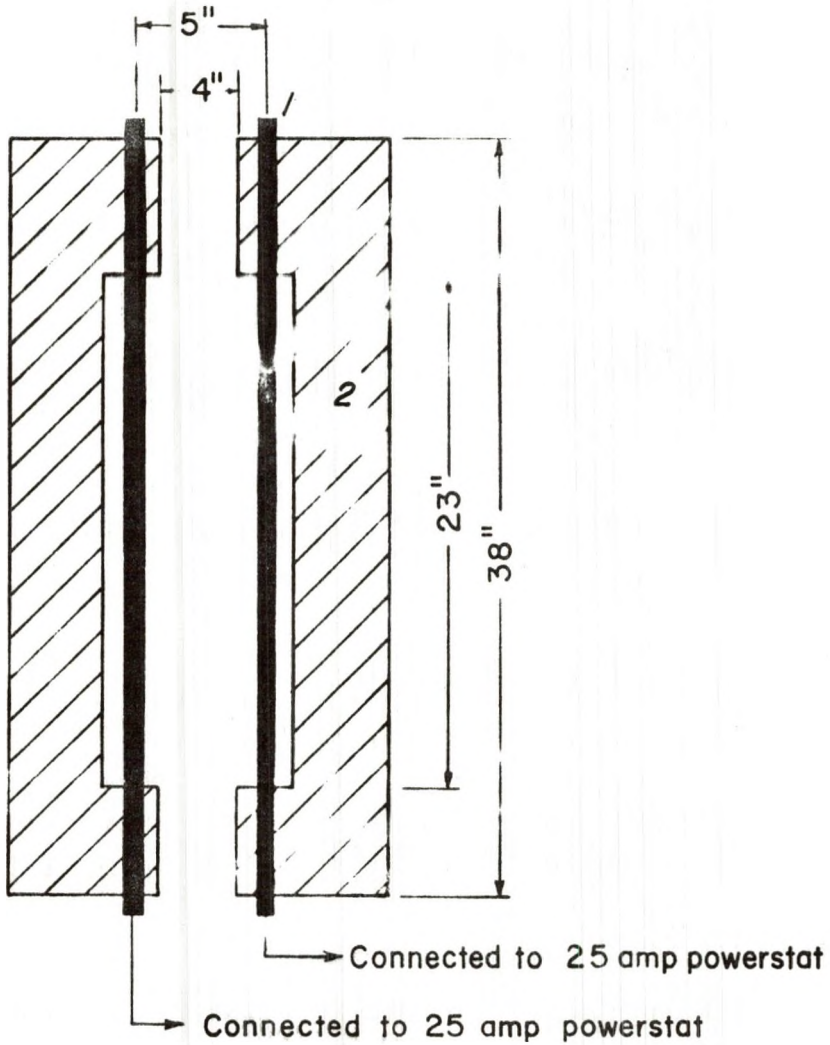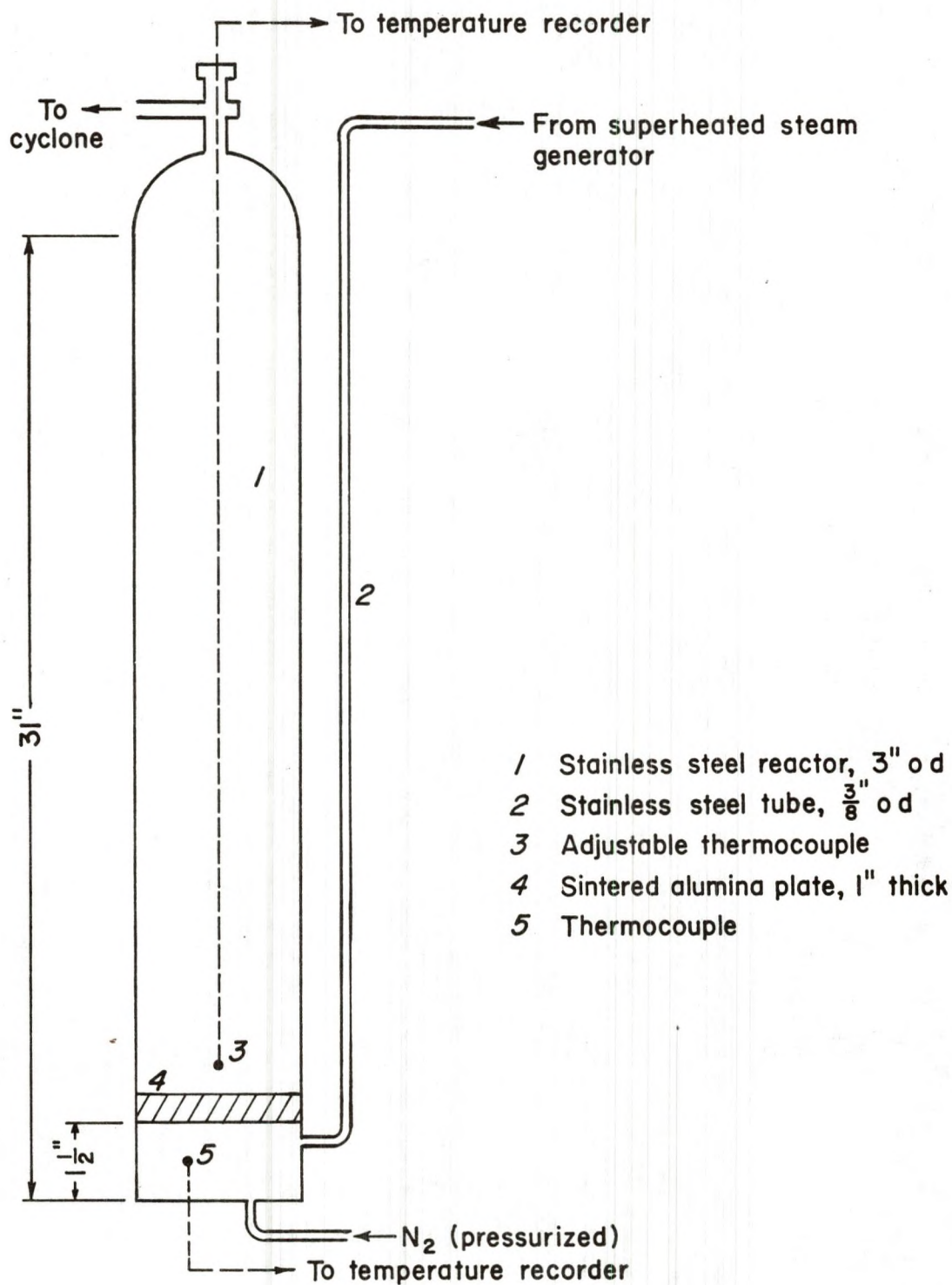s were raised slowly over that period of time to 1,700° F. When they reached 1,700° F, the reciprocal pump and the steam preheaters were started. The system was then allowed to heat until the steam in the reaction chamber was about 170° F higher than the desired reaction temperature and the system was stabilized. At 1,700° F, the linear flow rate of steam in the reactor was about .31 ft per second. This velocity went up or down with temperature difference, since the mass of steam fed was held constant.

To charge the reactor, the flow of steam was stopped, the thermocouple was removed, and the charger installed. After the valve of the charger was opened, a steel rod was used to tap the sides to prevent material from clinging to the walls. The charger was then removed, the thermocouple replaced, the feed pump turned on, and time measurements were begun.

During charging, about 10 percent of the material was blown out of the bed by steam and volatile matter released from the char. This material was immediately removed from the collection chamber so that it would not be mixed with the product. Generally, the bed temperature would reach the desired value by the time the collection chamber had been emptied. It then took only slight changes to the power supply to achieve uniform control of temperature. When the run was completed, nitrogen pressure was applied to the bottom to carry the product to the cyclone, which had been previously purged with nitrogen. The product was collected and placed in sealed jars to cool and await testing. A flow diagram is shown in figure 6.

MATERIALS TESTED
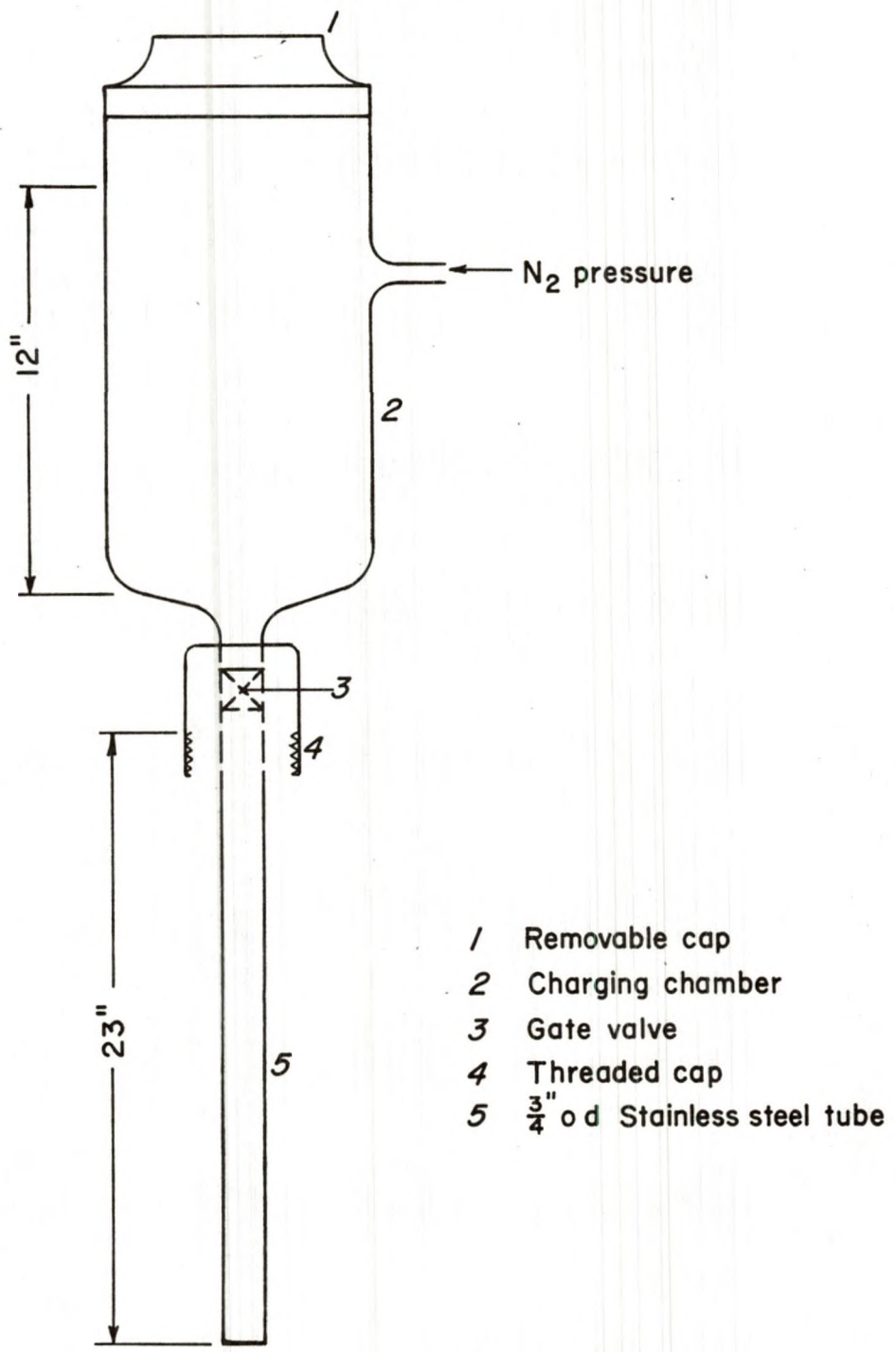
A char, which had been produced by carbonizing Beulah lignite

Fig 4 Details of charging device.
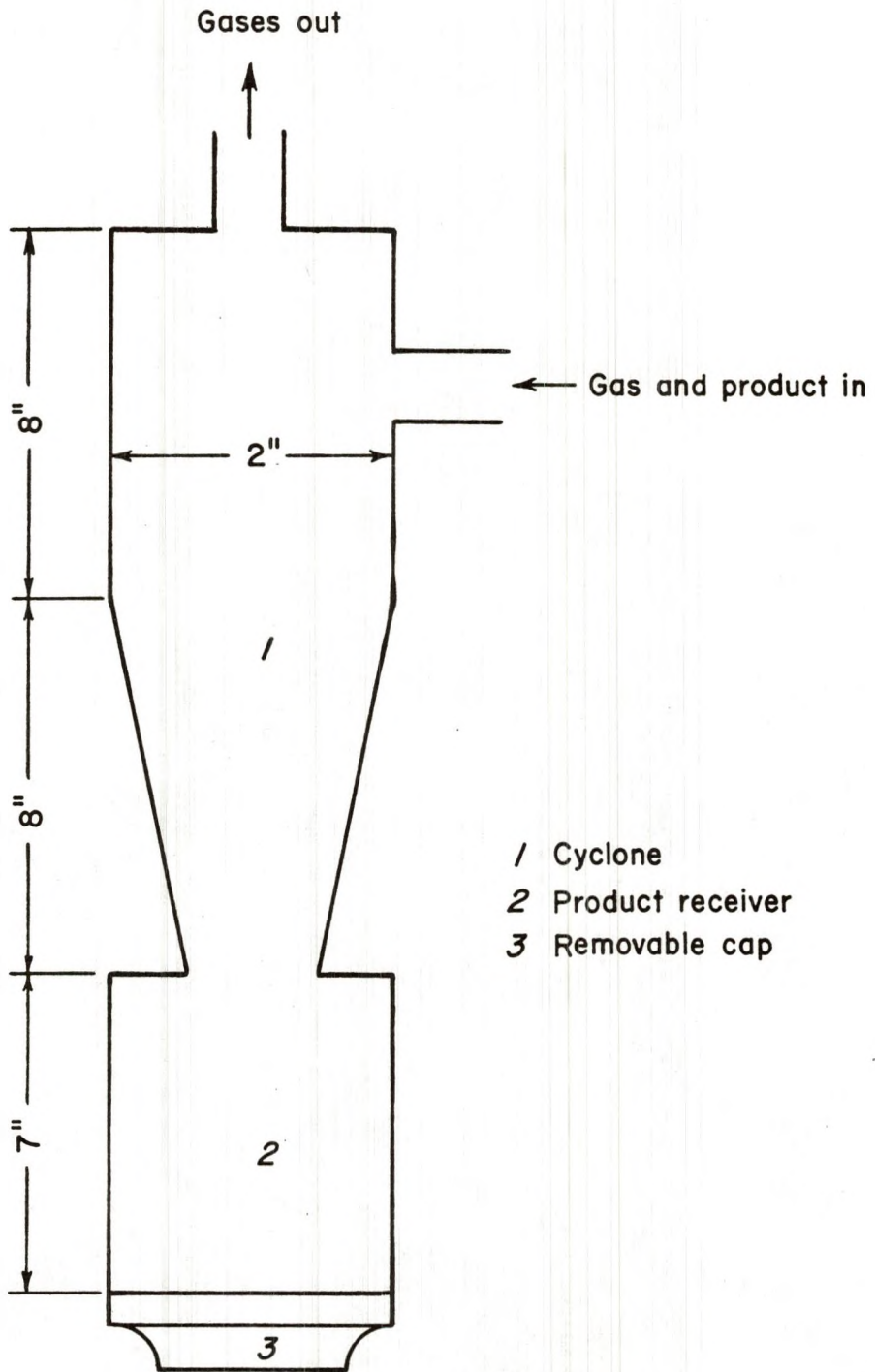
Fig 5 Details of cyclone and product receiver.

1 Steam generator
2 Steam superheater
3 Reactor heater
4 Reactor
5 Cyclone
6 Product receiver

Water in

Steam out

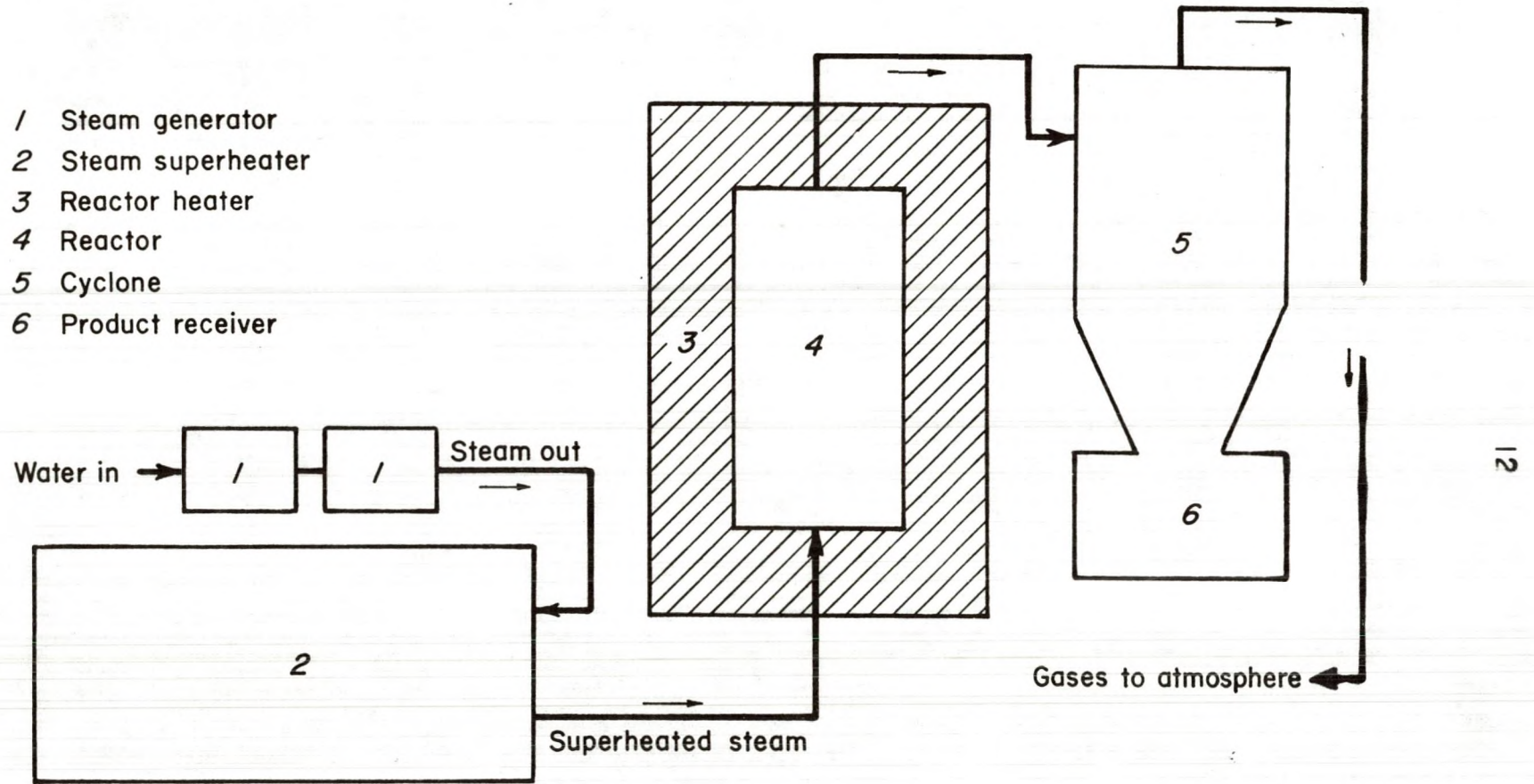Superheated steam

Gases to atmosphere

Fig 6 Equipment flow diagram.

at approximately 1,200° F, in an entrainment type carbonizer, was used as the starting materials for all tests. The proximate analysis of lignite and the char follows.

TABLE 1
Analysis of Beulah lignite and char, percent

	ash	moisture	volatile matter	fixed carbon
Beulah lignite	6.6	36.6	26.6	30.1
char	16.9	1.8	16.3	65.0

The char was screened into four different size fractions for use in the first design, but only one size was used in the second design.

Before charging, each char sample was heated at 500° F for 1 hour to remove any moisture that may have been adsorbed during storage and handling. In addition, the temperature differential between the char and the heated reactor was reduced somewhat.

ANALYSIS OF ACTIVITY OF PRODUCT

As liquid system carbons were to be the product, two liquid system tests were selected to evaluate activity. The iodine adsorption test[19] and the colorimeter test,[20] using malachite green, were chosen. The iodine test gives a good indication of an active carbon's odor adsorbing capacity and the colorimeter test determines its decolorization ability.

Iodine Adsorption Test - A stock solution of iodine containing 2.7 grams of iodine and 4.1 grams of potassium iodide per liter of solution was prepared. Actual concentration was determined and frequently checked by titrating, using sodium thiosulfate with a starch indicator. The reaction is:

$$2 \ S_2O_3^= + I_3^- \rightarrow S_4O_6^= + 3I^-$$
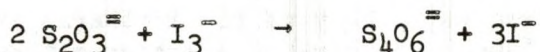
with the I_3^- complexing with the starch to form a deep blue color which gives a sharp end point when the I_3^- disappears.

Three weighed samples of each carbon were added to different erlenmeyer flasks each containing 100 ml. of stock iodine solution. These samples were 1 g, .6 g, and .2 g respectively. The flasks were then shaken for five minutes and the mixture filtered through

Colorimeter Test - One liter of absolute ethanol was mixed with
.86 grams of malachite green indicator. This mixture was then divided
into 50 ml. aliquots and placed in 250 ml. erlenmeyer flasks. One gram
of carbon product was added to one of the flasks and the flask was
shaken for 20 minutes. The solution was then filtered through 12 cm
No. 5 Whatman filter paper. Each filtrate was then tested using a
Bausch and Lomb, Spectronic colorimeter for light transmission at
482 millimicrons. These data are shown in appendix A, table 8, and
in figures 9 and 11.

DESIGN OF EXPERIMENT

A Latin square is an experimental design used to determine which
variables are significant in relatively few tests, and is usually used
in preliminary testing to screen variables. The analysis of variance
of the Latin square design only shows if a variable affects the results,
not how. The advantage of this design is that three variables can be
tested in the same number of tests as two variables, and an experimental
error term is obtained having sufficient degrees of freedom to
establish a reasonable critical "F" value at the significance level
chosen. This design and subsequent calculations are discussed by Wine.[22]

The design showing the levels of variables for the first series
of tests is shown in table 2.

Results from the original Latin square design was used to indicate
the significant variables and levels that give optimum test conditions.
Another test series was run to establish the best levels of the two
variables found to be significant. This series was run using a two-way,
three-level classification.[23] The design and levels are shown in table 3.

RESULTS AND DISCUSSION

Figures 7 and 8 indicate that three of the active carbons produced
during the first series had isotherms which were above the Darco isotherm.
These carbons were prepared at 1,450° F and 24 minutes residence time,
as shown on figure 7; and 1,750° F and 20 minutes, and 1,750° and 24 minutes
residence time as shown in figure 8. All three of these carbons appear,
from the plots, to be better than Darco, especially at lower concentrations.
Raw lignite and lignite char had isotherms which were much lower than
Darco or the active carbons produced during this study. The char isotherm
is shown in figures 7 and 8 while the raw lignite isotherm is not shown
because it is so low.

TABLE 3

Two-way classification design and levels of variables

Row Variable Residence Time, Min.	Column Variable (Temperature, °F)		
	1650	1700	1750
16	1	4	7
20	2	5	8
24	3	6	9

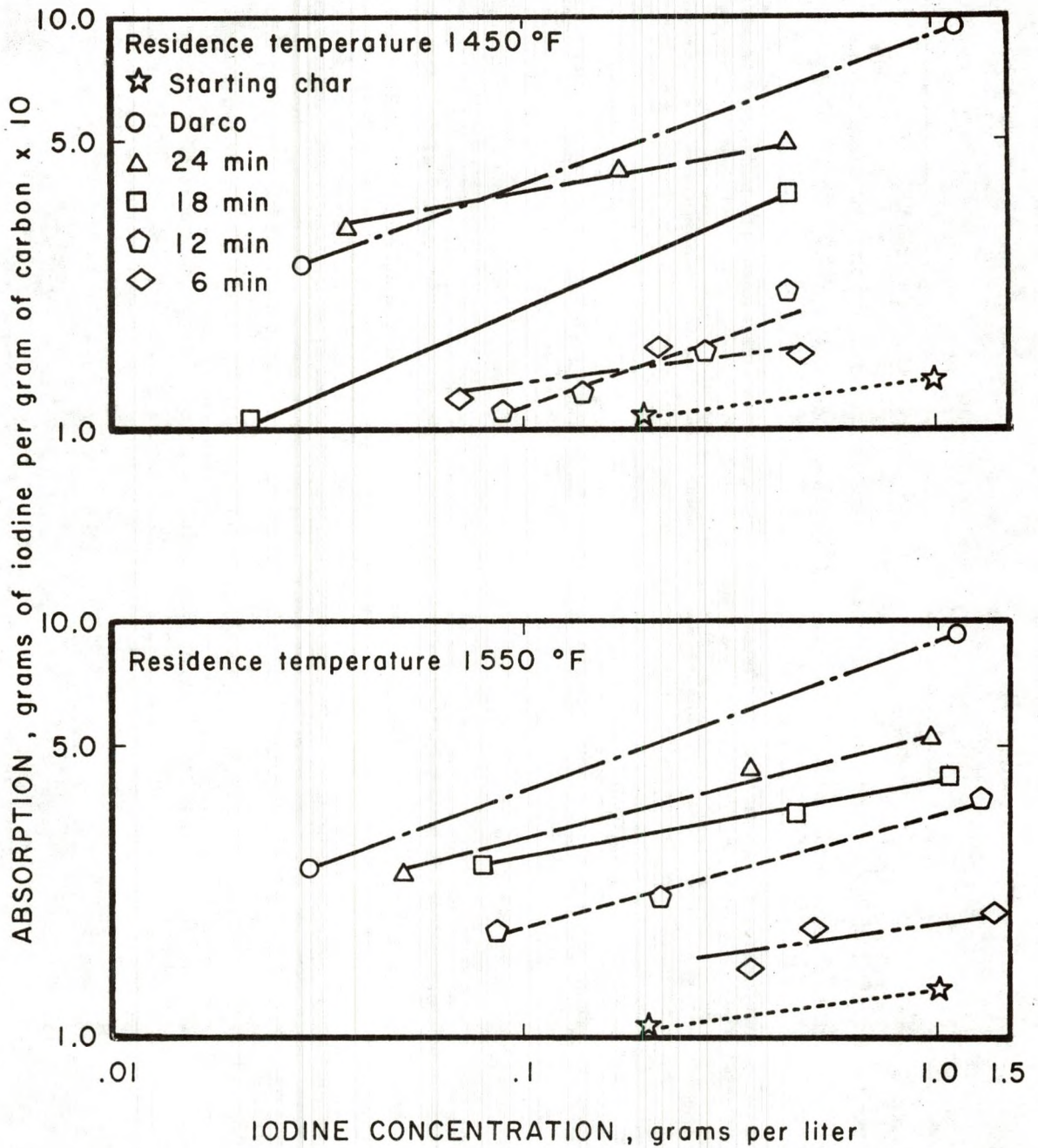All tests were run with −28 + 40 char particle size.

18

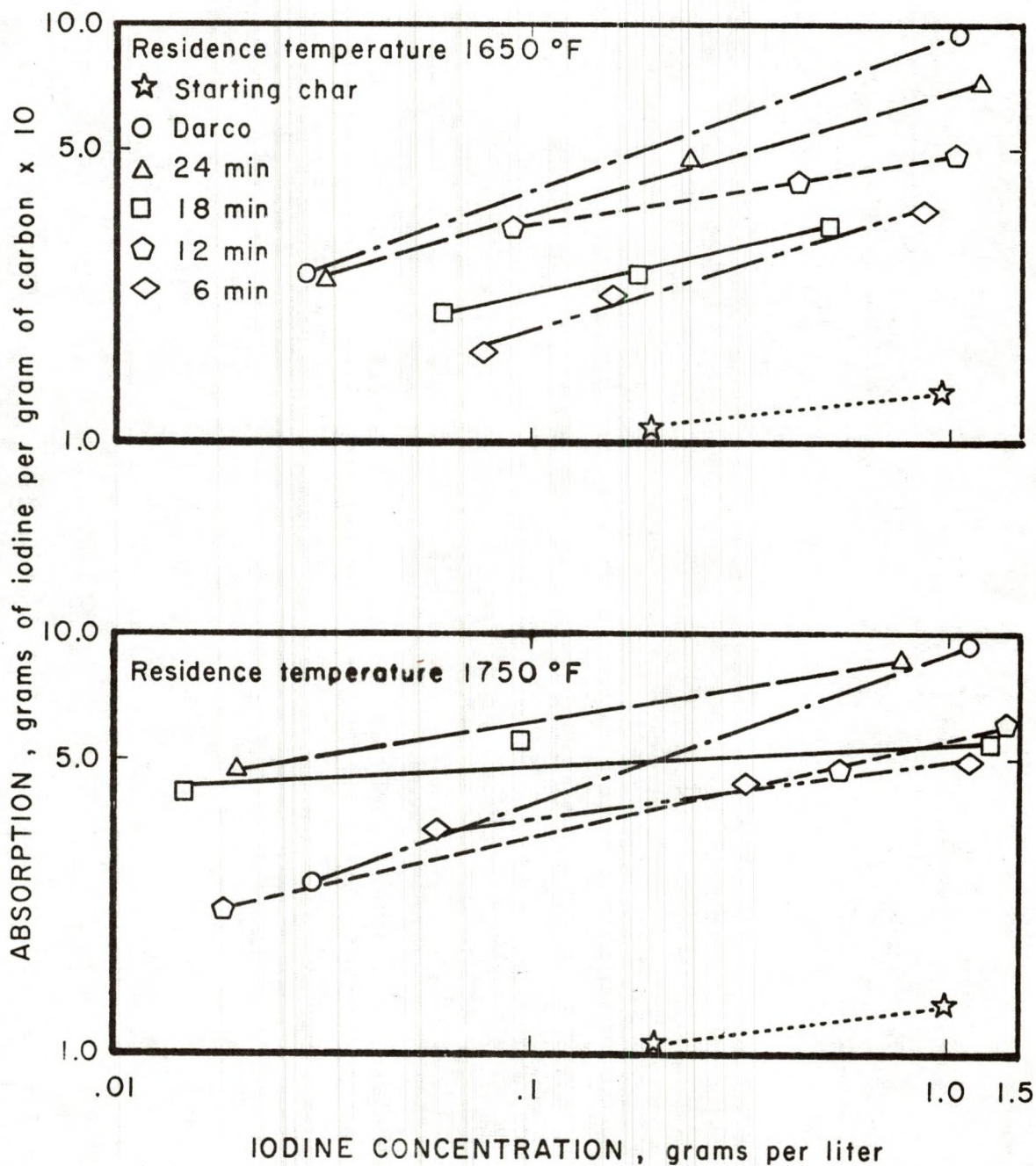Fig. 7.--Results of iodine test for Latin square design grouped by temperatures.

Fig. 8.--Results of iodine test for Latin square design grouped by temperatures.

Figures 7 and 8 also indicate that activity, as measured by the iodine adsorption test, increases with increasing temperature and increasing residence time. This observation is confirmed by the statistical analysis of variance which is shown in table 4. The table shows that the effects of temperature and of residence time were significant in the 95 percent confidence interval while the effects of particle size were insignificant. The value of σ_C^2 is greater than σ_R^2, indicating that residence time has a greater affect than temperature. The data used and the calculations made for this analysis are shown in appendix B, table 9.

Total sums for particle size indicate that activity is somewhat influenced by particle size, but analysis of variance does not confirm this observation at the 95 percent confidence interval. It is possible that there is some effect, which did not show in the present tests because of the limited degrees of freedom making it difficult to indicate a small effect. Additional testing might indicate significance, but the effect is small in comparison to that of the other variables.

The three results of the colorimeter test shown in figure 9 agree with the results depicted in figures 7 and 8. A general increase in transmittance as either temperature or residence time increased was noted. All of the carbons produced at temperatures greater than 1,650° F or at residence times longer than 12 minutes were superior to Darco for decolorization purposes.

An analysis of variance, as shown in table 5, agrees with the observations made about figure 9. It shows that, while particle size was insignificant, temperature was significant in the 95 percent confidence interval and residence time was significant at the 99 percent confidence interval, and again residence time had the greater σ_i^2.

As a result of analysis of variance, particle size was omitted as a variable in the second design. Temperature and residence time were studied at higher residence temperatures and longer residence times as these conditions were indicated to give the best activity.

Figure 10 shows the results of the second series of tests as measured by the iodine adsorption test. These plots do not indicate any definite trend as far as temperatures are concerned, even though the changes were statistically significant. There does seem to be a relationship between residence time and activity.

The analysis of variance in table 6 shows significance at the 95 percent confidence interval and residence time at the 99 percent confidence interval. All of the carbon produced at residence times greater than 16 minutes surpassed Darco in iodine adsorption at some concentration. Several were superior to Darco at all concentrations.
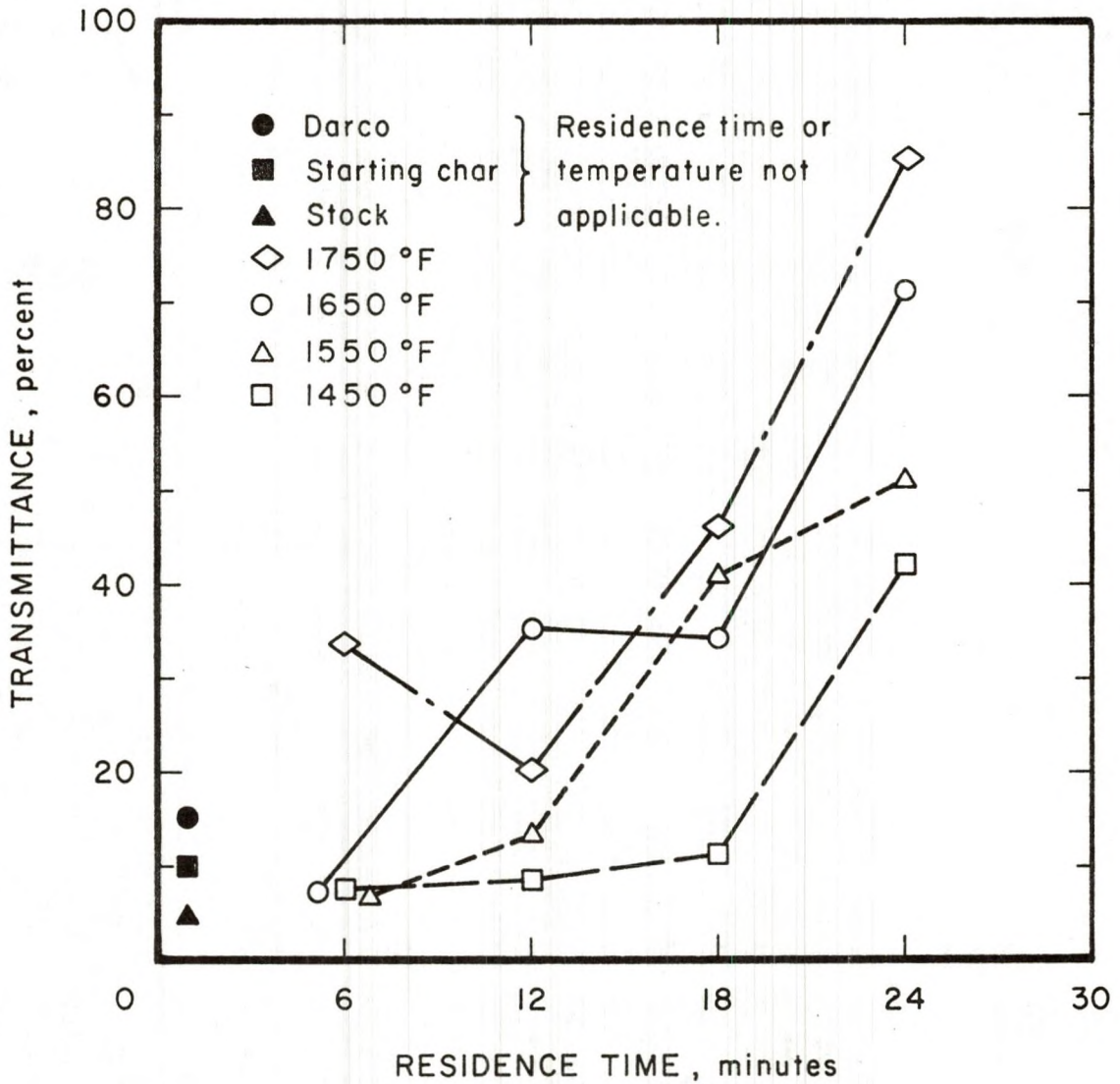
Fig. 9.--Results of colorimeter test for Latin square design.

TABLE 5
Analysis of variance
For colorimeter test--Latin square design

Source	S.S.	D of F	M.S.	F_{calc}	$F_{.05(3,6)}$[26]	$F_{.01(3,6)}$[27]	σ^2_i
Temp. (C)	1,856.19	3	618.73	5.22	4.76	9.78	125.04
Residence Time (R)	5,602.72	3	1,867.57	15.75	4.76	9.78	437.25
Particle Size (Tr)	243.19	3	81.06	.68	4.76	9.78	
Error	711.34	6	118.55	-----	-----	-----	
Total	8,413.44	15					

23
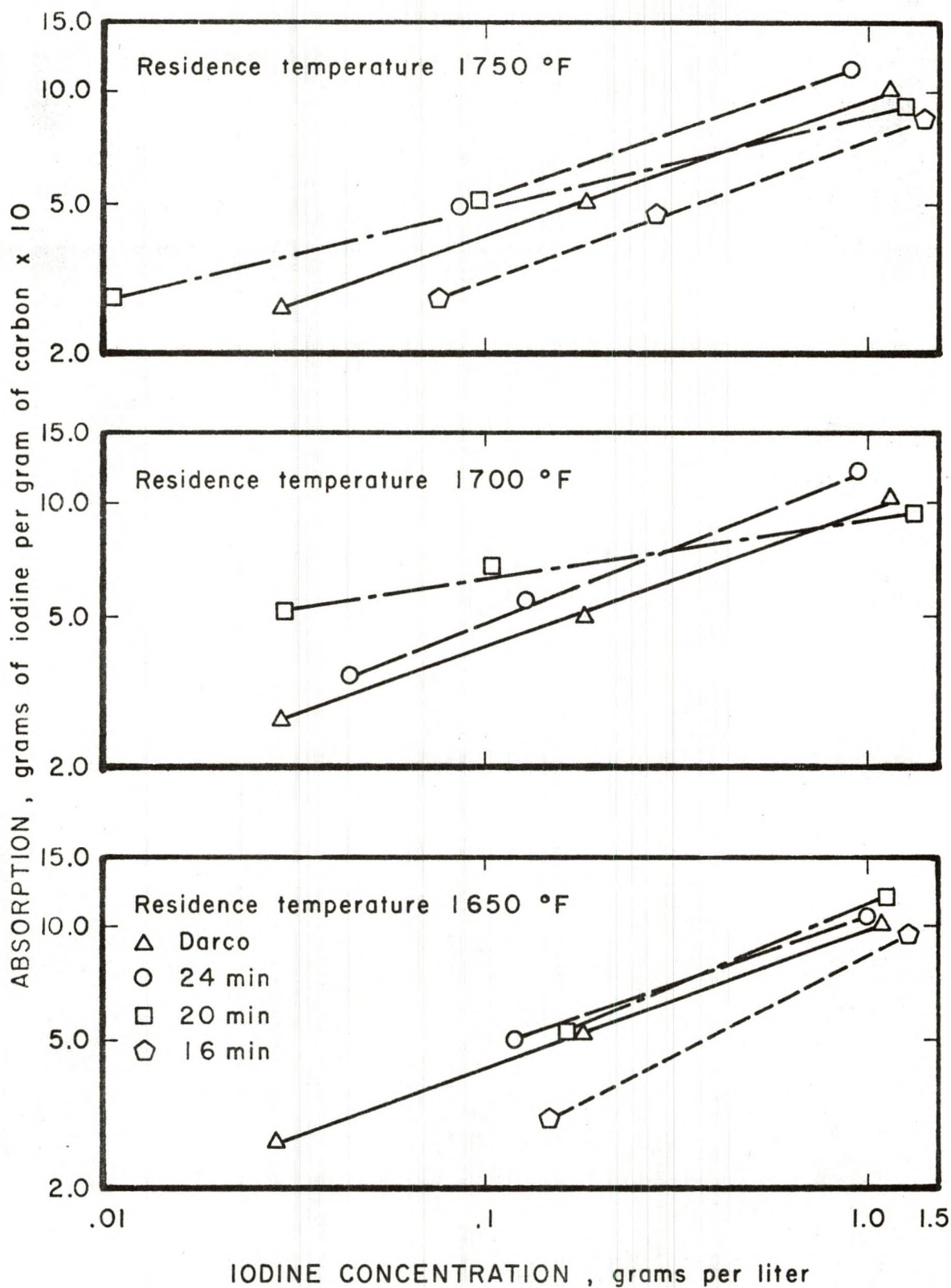
Fig. 10.--Results of iodine test for two-way classification design grouped by temperatures.

TABLE 6
Analysis of variance
for iodine test--two-way classification design [1]

Source	S.S.	D of F	M.S.	F_{calc}	$F_{.05(2,4)}$[28]	$F_{.01(2,4)}$[29]	σ_i^2
Temperature (col)	.78	2	.39	9.18	6.94	18.0	$.12 \times 10^{-2}$
Residence time (row)	9.67	2	4.84	113.88	6.94	18.0	1.60×10^{-2}
Error	.17	4	.0425				
Total	10.62	8					

[1] Data values x 10.
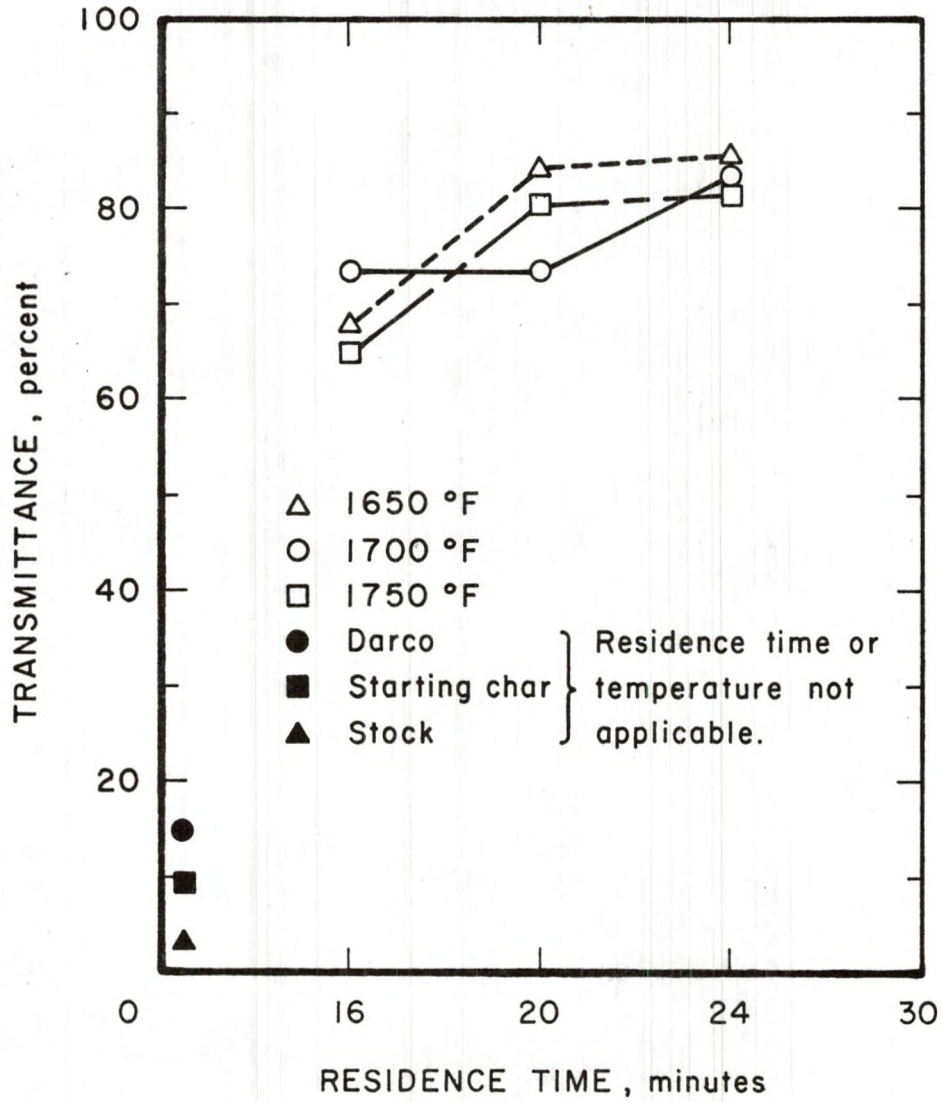
Fig. II.--Results of colorimeter test for two-way classification design.

TABLE 7
Analysis of variance
for colorimeter—two-way classification design

Source	S.S.	D of F	M.S.	F_{calc}	$F_{.05(2,4)}$ [30]	$F_{.01(2,4)}$ [31]	σ^2_i
Temperature (col)	13.6	2	7.8	.28	6.94	18.0	
Residence time (Row)	357.6	2	178.8	6.43	6.94	18.0	50.6
Error	108.4	4	27.1				
Total	479.6	8					

size on activity. Optimum conditions of each should be
determined.

(5) Activating lignite below the indicated optimum
temperature, but for longer residence times should be attempted.

(6) Differences in the ability of coal from different mines
to be activated should be studied.

(7) Steam is not the only activating gas. Oxygen, carbon
dioxide, and air should be used as activating agents.

(8) Pre-treatment of carbons with metalic chlorides often
affects the product. This could be tried on lignite.

(9) An attempt should be made to activate raw lignite
and dried lignite.

TABLE 8 continued

Run No.	Carbon No.	Activation Temp.	Residence Time, Minutes	Particle Size	Percent Ash	Percent Moisture	$\dfrac{g\ I_2}{g\ carbon}$ at .3 g/l	Percent Color Removed
1	5	1550	6	-20 + 28	10.22	6.78	0.190	3
1	6	1550	12	-28 + 40	23.36	5.19	.220	10
1	7	1550	18	-40 + 50	25.22	7.92	.345	37
1	8	1550	24	-6 + 20	31.51	3.65	.405	47
1	9	1650	6	-28 + 40	23.66	5.12	.255	4
1	10	1650	12	-40 + 50	28.47	4.89	.395	32
1	11	1650	18	-6 + 20	26.73	1.17	.280	30
1	12	1650	24	-20 + 28	29.01	3.34	.420	67

32

TABLE 8 continued

Run No.	Carbon No.	Activation Temp.	Residence Time, Minutes	Particle Size	Percent Ash	Percent Moisture	$\dfrac{g\ I_2}{g\ carbon}$ at .3 g/l	Percent Color Removed
2	5	1700	20	-28 + 40	36.22	.78	0.550	73
2	6	1700	24	-28 + 40	29.36	1.19	.660	85
2	7	1750	16	-28 + 40	43.22	1.92	.460	65
2	8	1750	20	-28 + 40	51.51	.65	.415	80
2	9	1750	24	-28 + 40	48.21	2.69	.725	82

$$SSC = \frac{(Totals\ for\ Columns)^2}{4} - \frac{56.7^2}{16}$$

$$SSC = \frac{1}{4}(11.0^2 + 11.6^2 + 13.5^2 + 20.6^2) - 200.93$$

$$SSC = 14.61$$

$$SSR = \frac{(Totals\ for\ Rows)^2}{4} - \frac{56.7^2}{16}$$

$$SSR = \frac{1}{4}(10.25^2 + 12.0^2 + 14.65^2 + 19.8^2) - 200.93$$

$$SSR = 13.0$$

$$SSTr = \frac{(Totals\ for\ treatments)^2}{4} - \frac{56.7^2}{16}$$

$$SSTr = \frac{1}{4}(12.7^2 + 12.95^2 + 16.05^2) - 200.93$$

$$SSTr = 1.97$$

$$SST = (Individual\ values)^2 - \frac{56.7^2}{16}$$

$$SST = 1.65^2 + 1.65^2 + 3.20^2 \ldots\ldots\ldots 5.20 + 7.05^2 - 200.93$$

$$SST = 34.11$$

$$SSE = SST - SSR - SSC - SSTr$$

$$SSE = 34.11 - 14.61 - 13.00 - 1.97$$

$$SSE = 4.53$$

Degrees of freedom for rows = No. of rows - 1
$$= 4 - 1 = 3$$

Degrees of freedom for columns = No. of column - 1 = 3

Degrees of freedom for treatments = No. of treatment - 1 = 3

Total degrees of freedom = (No. of rows) x (No. of columns) - 1 = 15

Degree of freedom for error = 15 - 3 - 3 - 3 = 6

36

TABLE 10
Data for table 5

Row Variable	Column variable (Temperature, °F)				
Residence Time, Min.	1450	1550	1650	1750	Totals
6	2 A	3 B	4 C	30 D	39
12	3 B	10 C	32 D	16 A	61
18	10 C	37 D	30 A	43 B	120
24	38 D	47 A	67 B	81 C	233
Totals	53	97	133	170	453

calculations for table 5

Total A = 2 + 47 + 30 + 16 = 95

Total B = 3 + 3 + 67 + 43 = 116

Total C = 10 + 10 + 4 + 81 = 105

Total D = 38 + 37 + 32 + 30 = $\frac{137}{453}$

$$SSC \ (temp) = \frac{53^2 + 97^2 + 133^2 + 107^2}{4} - \frac{453^2}{16}$$

$$= \frac{2809 + 9409 + 17,689 + 28,900}{4} - 12,825.56$$

$$= 14,681.75 - 12,825.56$$

$$SSC = 1,856.19$$

$$SSR = \frac{1}{4}(39^2 + 61^2 + 120^2 + 233^2) - 12,825.56$$

$\sigma^2 = 118.55$

$$\sigma^2_C = \frac{MSC - \;^2}{4} = \frac{618.73 - 118.55}{4} = 125.04$$

$$\sigma^2_R = \frac{MSR - \;^2}{4} = \frac{1,867.57 - 118.53}{4} = 437.25$$

$$\text{SSR} = 302.08 - 292.41 = 9.67$$

$$\text{SST} = 15.21 + 33.64 + 38.44 + 18.49 + 42.25 + 43.56 + 21.16$$
$$+ 37.82 + 52.56 - 292.41$$

$$= 010.62$$

$$\text{SSE} = 10.72 - 9.67 - .78 = .17$$

$$\text{MSC} = \frac{\text{SSC}}{2} = \frac{.78}{2} = .39$$

$$\text{MSR} = \frac{\text{SSR}}{2} = \frac{9.67}{2} = 4.84$$

$$\text{MSE} = \frac{\text{SSE}}{4} = \frac{.17}{4} = .0425$$

$$\text{FR}_{(calc)} = 4.84/.0425 = 113.88$$

$$\text{FC}_{(calc)} = \frac{.39}{.0425} = 9.18$$

$$\sigma^2 = 4.25 \times 10^{-4}$$

$$\sigma^2_C = \frac{\text{MSC} - 0.0425}{(3)(100)} - 1.2 \times 10^{-3}$$

$$\sigma^2_R = \frac{\text{MSR} - 0.0425}{(3)(100)} = 1.6 \times 10^{-3}$$

SST = 4,489 + 5,476 + 4,225

    7,225 + 5,329 + 6,400

    7,056 + 7,225 + 6,724 - 53,669.4

   = 54,149 - 53,669.4

   = 479.6

SSE = 479.6 - 357.6 - 13.6

SSE = 108.4

$\sigma^2 = 27.1$

$\sigma_R^2 = \dfrac{MSR - {}^2}{3} = 50.6$

20. Ibid, p. 321.

21. Daniels, R. K., and Alberty, F. Physical Chemistry.
     New York: John Wiley and Sons, Inc., 1961, p. 61.

22. Wine, R. L., Statistics for Scientists and Engineers.
     Englewood Cliffs, New Jersey: Prentice Hall, Inc., 1964, p. 642.

23. Ibid, p. 638.

24. Ibid, p. 638.

25. Ibid, p. 642.

26. Ibid, p. 638.

27. Ibid, p. 642.

28. Ibid, p. 638.

29. Ibid, p. 642.

30. Ibid, p. 638.

31. Ibid, p. 642.