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LOCAL OVERHEATING DURING GASIFICATION OF COKE WITH AIR

in a
FLUIDIZED BED

by
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of
Bachelor of Science
in
Chemical Engineering
from
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May 25, 1953

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Dear Sir:

In accordance with the regulations of the faculty, this thesis entitled "Local Overheating During Gasification of Coke With Air in a Fluidized Bed" is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Signature redacted

R. J. Weidman

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I. SUMMARY.

The writer has observed, by experimentation, the degree of local overheating that occurs during the gasification of metallurgical coke with air in a fluidized bed between the temperatures 1300-2100°F. with superficial velocities ranging 0.25-0.70 feet per second. The experimentation is of industrial importance, because the fluidized bed promises to eliminate the major overheating problems of present fixed bed methods of gasifying coke at high temperatures, due to thorough solids mixing during fluidization.

An earlier worker in the field, Paxton, found that serious local overheating occurred (causing failure of a stainless steel reactor) between 900-1150°F. with richer O₂ mixtures (21-35%). However, the results of the writer indicate only a mild overheating with air above 1900°F.; below this temperature, solids mixing in the 2"dia. x 18"dp. bed used was quite sufficient to distribute the large heat release at the bottom of the bed (inlet gas region).

The author concludes that solids mixing in the inlet gas region is the main problem to be solved in eliminating local overheating. Before a commercial size reactor is built, further experimentation to determine the optimum design for this region is desirable.

II. INTRODUCTION.

A. The Industry and This Investigation.

The long run increasing demand for CO₂, CO, H₂ and N₂ for synthesis gas and/or fuel, correspondingly stimulates the desire for cheaper production of these materials. At this time, reactions among O₂ from air, steam and coke in a fixed bed are used to produce these gases, which afterwards may be purified and processed as desired. This fixed bed method has a serious difficulty in that the highly exothermic reactions cause severe local overheating at the point of gas entrance to the fixed coke bed, which often results in a burnt-out grate or furnace wall and the formation of hard, fused clinkers.

The successful use of fluidization in the petroleum industry in burning deposited carbon off finely divided catalyst particles indicates that this method might solve the overheating problems mentioned above. A finely divided coke, with its enormous surface area, reacts much more rapidly than the lumps of a fixed bed gas producer, however. Thorough solids mixing must be maintained during fluidization, or "hotspots" will develop, just as in the fixed bed.

Before a commercial size gas producer can be successfully designed, additional data to that already in the literature, are needed. Since past experimental work indicates that the solids mixing will be a key factor in

the design, it is necessary that the designer know just how much assurance from hotspots is obtainable for a certain gas velocity, particle size, height:diameter ratio of the dense bed, etc. The intention of the author is to supplement the data concerning the degree of local overheating to be expected when reacting air with finely divided coke at temperatures and gas velocities of industrial practicability.

B. Related Investigations of the Past at M.I.T.

1. Review of Paxton's "Low Temperature Oxidation of Carbon". (4)

Paxton's objectives were (a) to obtain quantitative information concerning the burning of carbon particles in a fluidized bed and (b), to collect quantitative physical-chemical data on the carbon-oxygen system. O_2 partial pressure was controlled with CO_2 , CO , or N_2 diluent. Three types of carbon were used, namely, hardwood charcoal, metallurgical coke and Ceylon graphite. He worked in the temperature range $600-1000^{\circ}F.$, with superficial gas velocities between $0.4-0.6$ feet per second, at a total pressure of 1.1 atmospheres at the bottom of the reactor. The reactor was a 10 ft. long alloy steel pipe, 1.78 " inside diameter, with thermocouple wells and pressure taps through the pipe wall.

Concerning the mechanical performance of the fluidized coke bed, Paxton found that local overheating always occurred if the O_2 content of the feed exceeded 21% , due

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to insufficient solids circulation in the dense bed (height:diameter ratio was approximately 60). With air, however, continuous isothermal operation could be maintained, even at the highest temperatures investigated, about 1150°F. At 1150°F., all O₂ of the air was consumed, burning the coke carbon at about 3% per hour. Isothermal operation was quite sensitive to O₂ partial pressure at 1150°F.; when O₂ concentration was increased suddenly to 30%, a slow uncontrollable temperature rise started with the bottom of the reactor becoming 40°F. hotter than the rest.

Since the validity of Paxton's physical-chemical data depended on the existence of continuous isothermal conditions within the dense bed, he made experimental tests and various heat release-heat transfer calculations to prove that, in fact, isothermal conditions did exist in the dense bed for all O₂ partial pressures at temperatures below 900°F, under which conditions the greatest part of the data were taken. However, he did show with calculations that at higher temperatures (1800°F.), the rate of heat release from a particle bathed in O₂ rises more rapidly than does the rate of heat transfer to the surroundings (also at 1800°F.), concluding that an individual particle's temperature can rise to a high level under such conditions - limited not by chemical resistance, but rather by inward O₂ diffusion rate.

Concerning the physical-chemical data, Paxton found the CO/(CO+CO₂)^{mol} ratio in the product gas to be constant and

equal to 0.24 for all carbon types below 1000°F., but decreasing rapidly at higher temperatures. He concluded that both CO and CO₂ were primary products of combustion.

Data collected between 840-950°F. with coke and O₂ diluted with CO₂ or N₂ show that the specific carbon gasification rate was proportional to the number of mols of carbon in the bed, the log mean average partial pressure of O₂ in the dense bed and the temperature of the dense bed (other conditions, such as particle size distribution, etc. were held constant). Paxton correlated the rate data with the equation

$$k = Ae^{-B/RT}$$

where

k = specific reaction rate (fraction carbon gasified per minute per log mean average atmospheres of O₂ partial pressure).

A = constant = 4.5 x 10⁵ (same units as those for "k"). for the specific metallurgical coke used.

B = constant = 52,200 Btu/ lb. mol. for the specific metallurgical coke used.

R = gas constant = 1.987 Btu/ lb. mol. R⁰.

T = reaction temperature (R⁰)

e = base of natural logarithms.

Paxton recorded that net carbon gasification rates with CO diluent were more than twice the corresponding rates with CO₂ and N₂ diluents for O₂ partial pressures between 0.05-0.21 atm. He also recorded that CO leaving was always greater than CO entering for runs made with CO diluent and O₂ concentrations less than 34%, despite

high net carbon gasification rates.

2. Review of McBride's "Gasification of Carbon by CO₂ in a Fluidized Bed". (2)

McBride's objectives were (a) to study the reaction rate and (b), the mechanism of the reduction of CO₂ to CO by carbon, with main variables of CO₂ and CO partial pressure and carbon type (reactivity). He worked in the range of 1400-2000°F., at about 1.1 atm. total pressure in the bottom of the reactor. The batch-type reactor, itself, was quite similar to the one used by Paxton, but only 7 ft. tall.

McBride correlated the rate data with

$$-\frac{dn}{dW} = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}}$$

where

n = CO₂ passing any point within the dense bed, lb. mols./min.

W = weight of carbon in the dense bed, lb. atoms.

P_{CO₂}, P_{CO} = partial pressure of CO₂ and CO, respectively above the dense bed, atm.

k₁, k₂, k₃ = Ae^{B/RT}, where (for the metallurgical coke used)

	A	B
$\left(\frac{k_1}{\text{lb. atom C in bed}} \right) \times 10^4$ (lb.mols./min.atm.) x 10 ⁴	8.38 x 10 ⁹	-86,200
k ₂ (atm.) ⁻¹	0.0114	27,700
k ₃ (atm.) ⁻¹	0.206	11,500

T = reaction temperature, R° .

R = gas constant, Btu/ lb. mol. R° .

e = base of natural logarithms.

It is seen that $\frac{dn}{dW}$ is equivalent to "fraction carbon gasified as CO per minute".

The above correlation equation indicates that the rate of CO_2 reduction, $\frac{dn}{dW}$, is retarded by CO (under the operating temperatures used), moreso at lower temperatures (about $1600^{\circ}F.$), which is contrary to the findings of Paxton at a lower temperature range ($600-1000^{\circ}F.$).

McBride did make one run with coke and O_2-N_2 mixtures ($O_2:N_2$ mol ratio equalled 0.22) at four temperature levels (1475° , 1600° , 1775° and $1900^{\circ}F.$). He found that the appropriate correlation equation would predict the CO formation rate, assuming that the O_2 formed CO_2 immediately at the bottom of the bed.

C. Purpose of This Investigation.

The purpose of this investigation is to determine experimentally the degree of local overheating to be expected in a bed of coke fluidized in air at $1350-2150^{\circ}F.$ The effect of superficial gas velocity and operating temperature on the formation of "hotspots", if any, will be studied. The mechanical performance of the bed will be studied in view of the findings of Paxton.

McBride's data for O_2-N_2 mixtures with coke will be compared with those of the writer.

III. EXPERIMENTAL PROCEDURE.

A. General Conditions.

The experimental work was carried out under the following conditions:

- 1. Reaction temperature: 1300-2100°F.
- 2. Superficial gas velocity: 0.25-0.70 FPS.
- 3. Reactant gas: air (approximately 21% O₂; 79% N₂).
- 4. Carbon type: metallurgical coke (from the same batch as that used by McBride and Valleroy⁽⁵⁾.)
- 5. Particle size distribution:

U.S. Series Mesh No.	Per Cent.
-40	0.7
+40-60	20.2
+60-80	43.2
+80-100	27.1
+100-140	8.8
	<u>100.0%</u>

- 6. Depth of dense bed: 17.5-19.5 inches (height:diameter ratio \cong 9).

B. Apparatus.

The reactor consisted of a lagged, stainless steel pipe, 2.065" I.D. x 50" high, with a removable gas inlet section (see Figs. 1 and 2, pp. 9 and 10). The inlet section contained a 200 mesh stainless steel screen and a "calming section", which helped distribute the entering air more uniformly than a mere taper at the bottom of the reactor. (This effect was studied by Ornea⁽³⁾, who used metallurgical coke with pure O₂). A 3" long x 1 1/4" dia. pipe, with a removable cap, welded at an angle to the top of the reactor,

FIGURE 1

DIAGRAM OF APPARATUS.

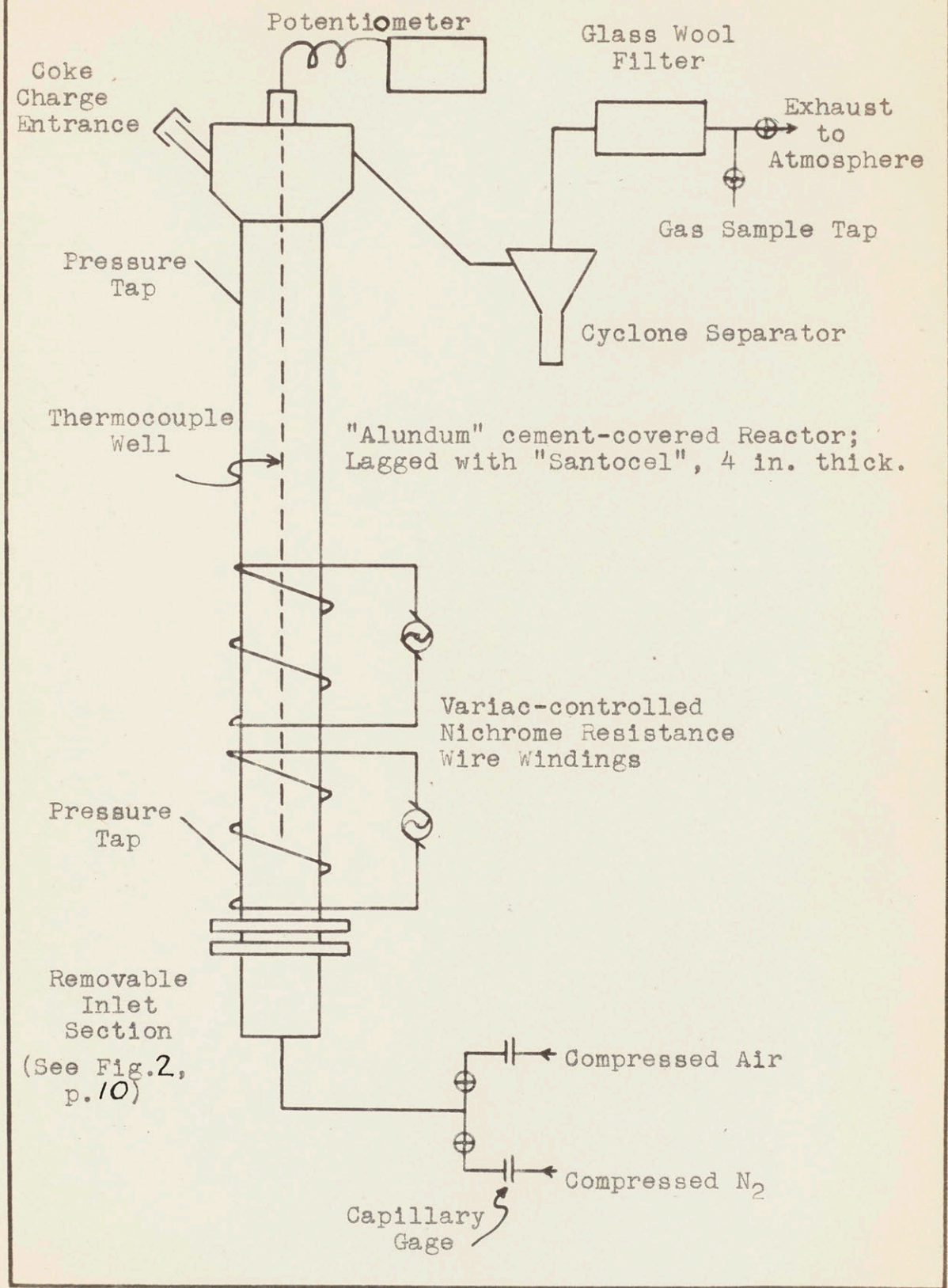
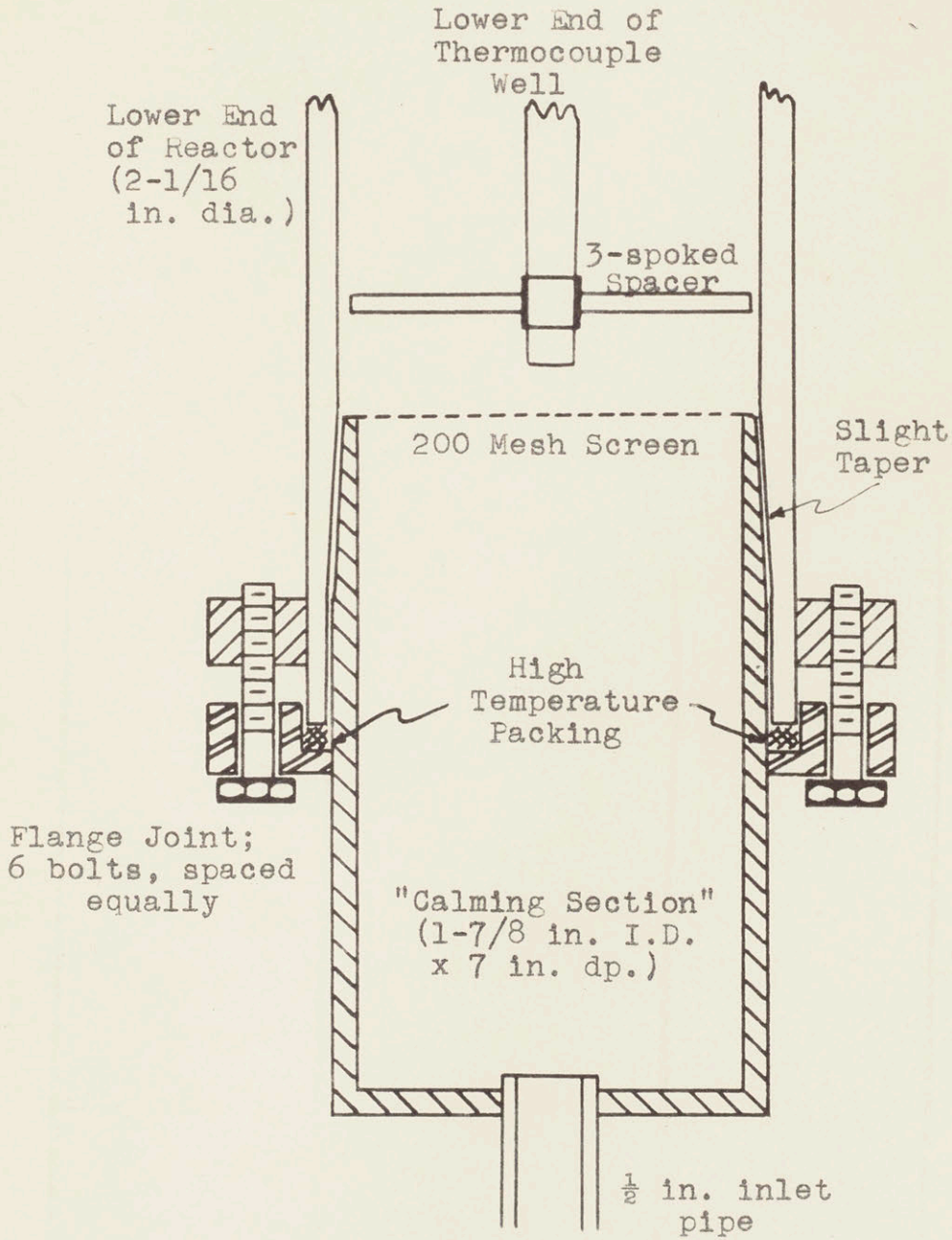


FIGURE 2

DETAILS OF REMOVABLE INLET SECTION



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provided an entrance for the solid charge. A small glass cyclone separator and a glass wool filter collected the fines carried over. Cylinder N₂ provided an inert gas for fluidizing the coke while heating the bed to reaction temperature by means of electrical energy supplied to the two Nichrome wire windings around the Alundum cement-covered reactor pipe. Electrical energy input was controlled by means of variacs. (Note: the lower resistance wire winding heated the 17" of pipe above the inlet screen, which contained essentially all the dense coke bed. The energy input to the upper winding was constant during the entire experimentation; temperature of the dense bed was controlled by changing the energy input to the lower winding, only). The reactant gas, air, was supplied from cylinders, also. Both N₂ and air flow rates were controlled by means of manually-operated pressure regulators and measured by capillary tube gages.

Temperature within the bed was measured by Chromel-Alumel thermocouples (20 gage) inserted through the top of the reactor along the axis of the pipe. An automatic Brown "Elektronik" temperature recorder was used for the first run only; a manually-operated potentiometer was used during the remaining runs.

The thermocouple arrangement was altered several times in an attempt to measure temperature variation within the dense bed as accurately as possible with minimum time delay. The best arrangement found consisted of seven thermocouples, 3" apart, sheathed by a stainless steel

tube 9/16" O.D. x 1/16" wall thickness, tapered starting 8" above the bottom end to a smaller cross sectional area at the bottom (about half the cross sectional area of that of the tube, itself), in order to minimize the fraction of the cross sectional area of the inside of the reactor occupied by the thermocouple well. The bottom end of this sheath was centered along the axis of the reactor about $\frac{1}{2}$ " above the inlet screen. The first thermocouple was located about 3/4" above the inlet screen. This arrangement was used for Runs 4 through 7. (See Table 1, p. 15, under column headed "Remarks" for description of thermocouple arrangement used in Runs 1 through 3).

C. Mechanics of a Run.

The empty reactor was brought to a temperature about 100-200°F. higher than the reaction temperature desired. Then N₂ was placed on stream at about the superficial velocity desired. Then the solid charge was admitted and the bed allowed to reach near-thermal equilibrium (temperature crawl rate of about 0.5 F°/min.) at the desired initial reaction temperature and superficial gas velocity. (Electric energy input was not changed afterwards). At this time, the N₂ was replaced with an air stream at the desired superficial velocity. Data on temperature and superficial velocity were taken about every twenty minutes until the bed again reached ^{near-}thermal equilibrium. Gas samples were taken before and/or after near-thermal equilibrium, as desired. After near-thermal

equilibrium had been reached, the run was terminated by replacing air with N₂ and turning off the electrical energy input. When the bed had cooled to near-room temperature, the N₂ was turned off, the inlet section was removed and the residue was collected and weighed. (Fines carried over were of negligible weight). The residue was observed visually for signs of ash and ash agglomeration.

D. Data Recorded During a Run.

1. Time (min.)
2. Individual thermocouple potentials (millivolts).
3. Pressure drop across N₂ and air capillary gages (in. of Hg.).
4. Line pressure on downstream side of the capillary gages (in. of Hg.).
5. Heating coil variac settings. (Variacs were calibrated with their respective coils according to Variac Setting vs. Electrical Energy Input).
6. (Occasionally) Pressure drop across the dense bed and the line pressure at the top of the reactor (in. of Hg.).

IV. RESULTS.

Table 1 tabulates seven representative data points for each of the seven runs made. This tabulation shows clearly the temperature and superficial gas velocity conditions as well as the temperature variation that existed in the dense coke bed during each run. Remarks are made concerning thermocouple arrangement to point out that the first three runs were made with slightly different apparatus than that with which the last four runs were made.

Figure 3 shows the comparison of the time histories for all runs, plotting the figures from Table 1 headed "Increase in Avg. Dense Bed Temperature Since Time=0" vs. "Time".

Table 2 tabulates the exit gas composition for the two or three samples taken during Runs 3, 5 and 7. The K_p ratio,

$$K_p = \frac{P_{CO}}{P_{CO_2}}$$

is calculated and the corresponding ratio at equilibrium (at the average dense bed temperature) is tabulated for comparison to indicate proximity to equilibrium.

Figure 4 illustrates the variation of temperature in the lower region of the dense bed during Run 7.

Run No.	Time (minutes)	Superficial Velocity (ft./sec.)	Avg. Dense Bed Temperature (F°)	Deviation of Individual Thermocouple Temperature from the Avg. Dense Bed Temperature (F°)							Avg. Deviation (F°)	Increase in Avg. Dense Bed Temp. Since Time=0. (F°)	Electrical Energy Input (Watts) and Weight of Residue (Grams)	REMARKS
				1	2	3	4	5	6	7				
1*	0	0.47	1335								0	780	3 thermocouples, 8" apart, used inside stainless steel tube (3/8" O.D.) sheath. Bottom couple 5/8" above 200 mesh screen. "Elektronik" temperature recorder used. No ash formation noticed.	
	10		1397								62	WATTS		
	30		1465								130			
	60		1535								200			
	100		1585								250			
	140		1620								285			
	180	0.54	1640								305			
				ESTIMATED							±2			
2	0	0.25	1314	-4	-4	-9	-9	0	+13	+87	-7	0	730	7 couples, 3" apart, used. Tips exposed to hot coke. All couples exposed and were shorted to each other by coke & cement used to bind them together. No ash formation noticed.
	12		1367	-14	-5	-9	-13	-9	+4	+61	-9	53	WATTS	
	21		1389	-5	-5	-5	-5	0	+9	+61	-5	75		
	40		1428	-8	+5	0	-4	+5	+9	+49	+5	114		
	85		1495	0	0	0	0	0	+9	+36	+2	181		
	135		1549	-5	0	+9	-5	0	+4	+22	+4	235		
	160	0.27	1558	-9	0	-5	0	0	+4	+22	-3	244		
		Avg →		-6	-3	-5	-5	-2	+7	+48	±5			
3	0	0.26	1362	-22	-22	BROKEN THERMOCOUPLE	-17	-7	+18	+96	-15	0	730	7 couples, 3" apart, sheathed by 0.01" nickel, used. Nickel worn through by heat & abrasion. All couples shorted by coke. Sandy, light-brown, partially fused ash found on screen and in residue.
	11		1411	-5	0		-5	-5	+4	+44	-4	49	WATTS	
	30		1455	-5	-5		-5	+4	+4	+31	-5	93		
	60		1499	0	0		+5	-4	+5	+18	+3	137		
	92		1531	0	0		0	0	+9	+9	+2	169		
	315		1589	-9	-4		-4	-4	+18	+26	-8	227	440	
	380	0.30	1589	+5	+5		-18	+5	0	+18	-7	227	GRAMS	
		Avg →		-7	-5	-8	-6	+8	+35	±6				
4	0	0.27	1662	-10	0	0	+5	+5	0	-12	3	0	990	7 couples, 3" apart, *** sheathed by stainless tube (1/16" wall). Sandy, light-brown, partially fused ash found on screen and in residue.
	10		1709	0	0	0	0	+9	+5	+5	+2	47	WATTS	
	20		1737	0	-5	0	0	0	0	-52	-1	75		
	40		1779	0	0	0	0	0	-4	-61	-1	117		
	84		1826	-4	0	0	0	0	0	-56	-1	164		
	126		1850	0	0	0	0	0	0	-61	0	188		
	180	0.33	1869	0	0	0	0	0	0	-61	0	207	520	
		Avg →		-2	-1	0	+1	+2	+1	-44	±1		GRAMS	
5	0	0.53	1643	-9	-4	0	0	0	0	-18	-2	0	990	Same remarks as for Run 4.
	10		1699	-4	0	0	0	0	0	-4	-1	56	WATTS	
	20		1737	+5	+5	0	0	-5	0	-14	+3	94		
	40		1784	0	0	0	0	0	-5	-9	-1	141		
	80		1841	0	+4	0	0	0	0	-10	+1	198		
	100		1855	0	0	0	0	0	0	-10	0	212		
	220	0.61	1893	-4	0	0	0	0	0	-28	-1	250	390	
		Avg →		-3	+2	0	0	-1	-1	-13	±2		GRAMS	
6	0	0.32	1803	0	0	0	+5	+5	-24	-94	-6	0	1040	Same remarks as for Run 4. 1/2" thick, fragile ash formation found on top of screen.
	10		1845	-4	-4	0	-4	0	-23	-117	-6	42	WATTS	
	30		1884	+5	0	+5	+5	+5	-10	-123	+5	81		
	60		1927	+5	+10	+5	+5	+5	-19	-129	+8	124		
	110		1970	+5	+15	+15	+9	+15	-24	-139	+13	167		
	180		2028	+10	+10	+10	+5	+5	-48	-168	-15	225		
	210	0.35	2028	+20	+10	+10	+10	+10	-53	-168	+16	225	500	
		Avg →		+8	+7	+6	+6	+6	-29	-134	±10		GRAMS	
7	0	0.60	1803	-5	+5	+5	-5	0	-5	-52	-4	0	1145	Same remarks as for Run 4. 3/4" thick, fragile ash formation found on top of screen. Pipe scale flakes also found.
	12		1860	-5	+5	+5	0	-5	-5	-29	-4	57	WATTS	
	30		1908	-5	+9	+5	0	-5	0	-24	+4	105		
	60		1970	+10	+10	+10	-9	-5	-5	-24	+8	167		
	120		2073	-5	+5	+5	-10	-5	0	-55	-5	270		
	180		2103	-70	+30	+25	+10	+15	+20	-50	+28	300		
	260	0.68	2118	-191	+45	+40	+25	+30	+30	-95	-60	315	320	
		Avg →		-41	+18	+14	+8	+9	+9	-47	±16		GRAMS	

*Run 1 used 700 grams coke charged; remaining runs used 600 grams.

**Number 7 thermocouple excluded from average, since it was above dense bed.

***Number 1 couple was 3/4" above screen; number 2 was 3 3/4" above screen; number 3 was 6 3/4" above, etc.

TABLE I

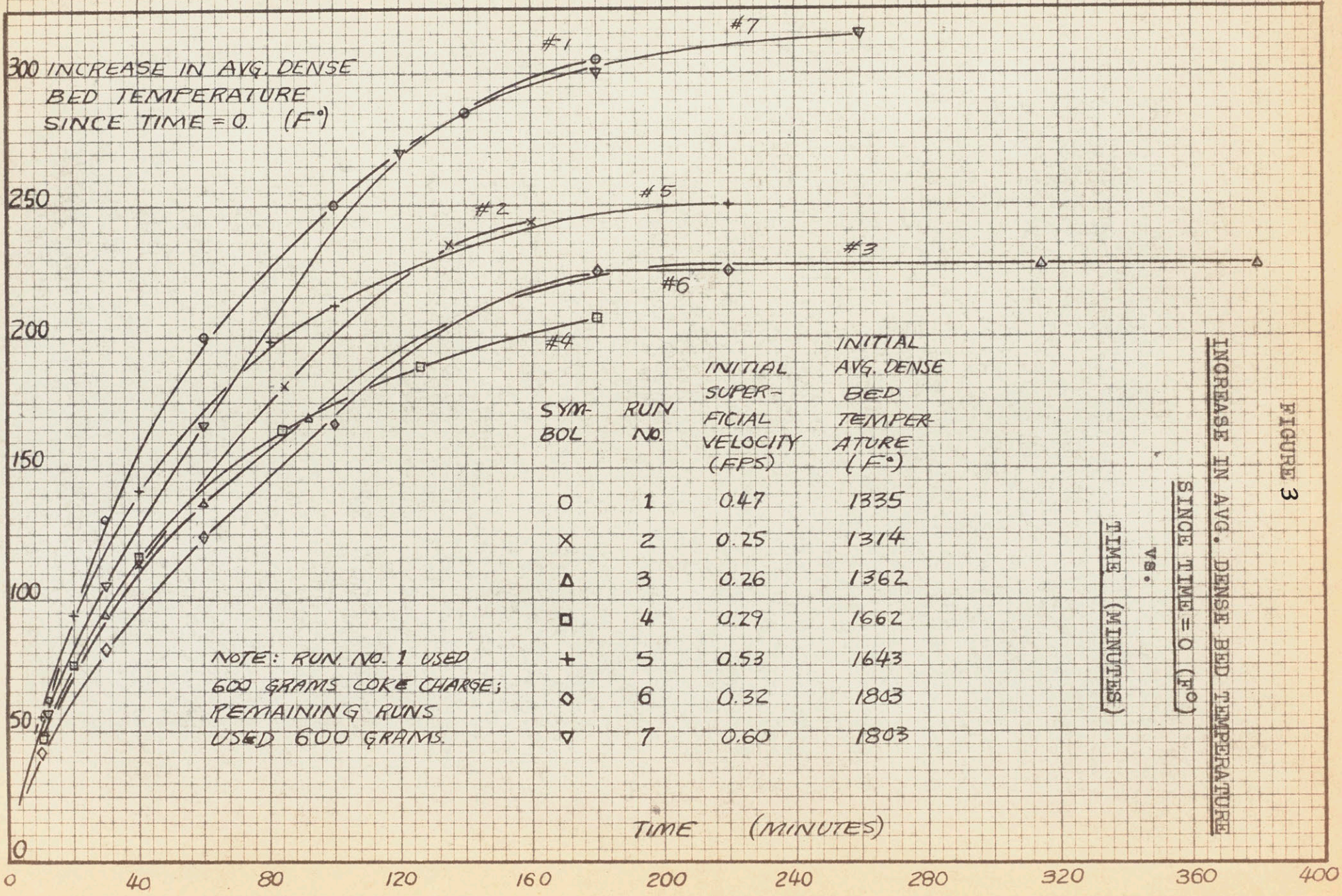


FIGURE 3

TABLE 2.

Run No.	Time (min.)	Superficial Vel. (FPS)	Avg. Dense Bed Temp. (F°)	Exit Gas Analysis*				K_e^{**}	
				CO ₂	CO %	O ₂	N ₂	$\frac{P(\text{CO})^2}{P(\text{CO}_2)}$ (atm.)	$\frac{P(\text{CO})^2}{\bar{P}(\text{CO}_2)}$ (atm.)
3	85	0.26	1525	16.76	7.06	0.00	76.19	0.0297	12.2
	321	0.30	1589	15.67	8.53	0.22	75.59	0.0463	21.8
	381	0.30	1589	15.12	9.58	0.00	75.30	0.0607	21.8
5	85	0.53	1847	7.97	21.07	0.11	70.85	0.557	158
	225	0.61	1893	7.53	21.81	0.11	70.55	0.630	222
7	243	0.60	2110	0.78	33.25	0.11	65.86	14.15	860
	265	0.68	2118	1.09	32.80	0.11	66.00	9.58	930

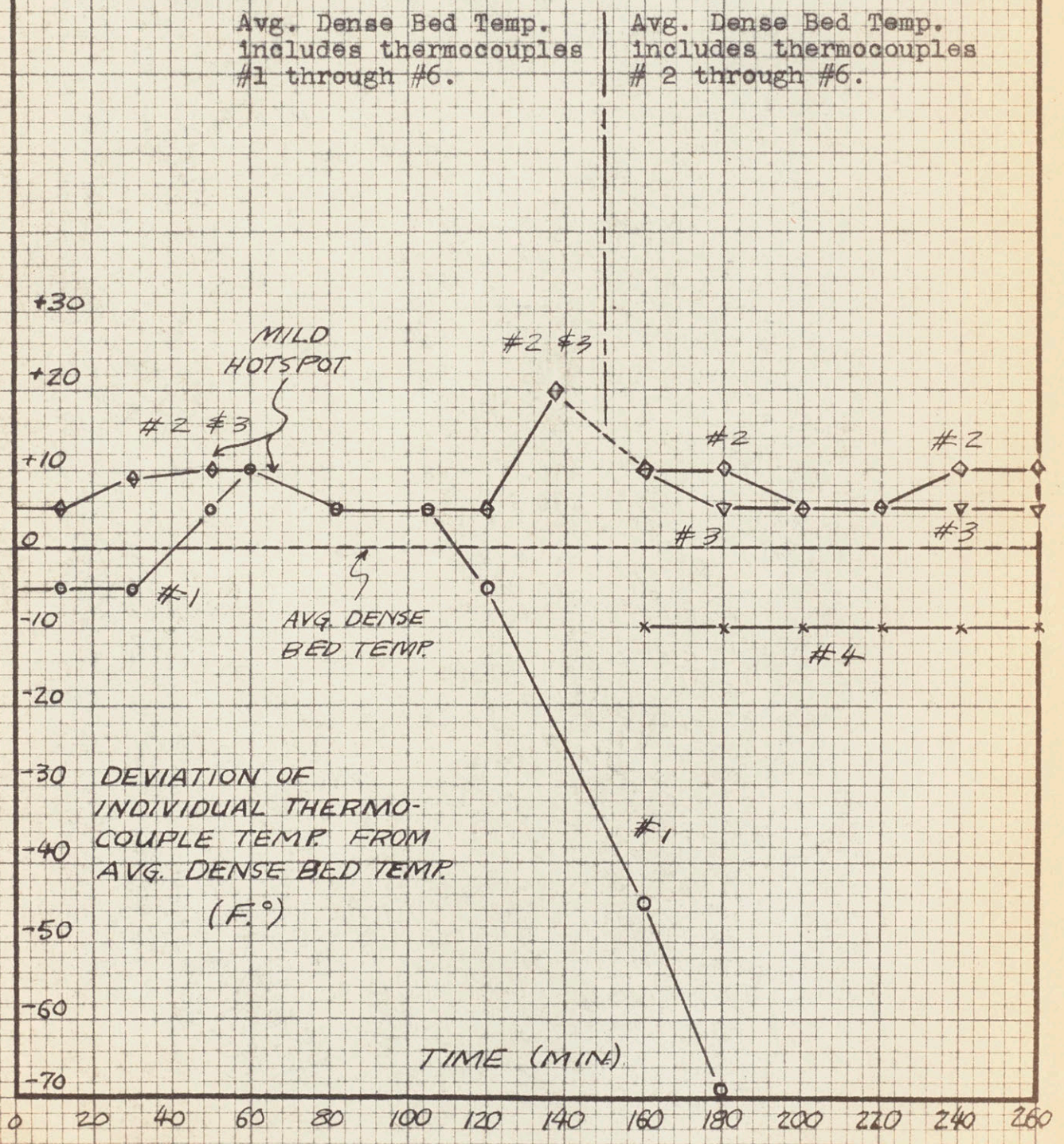
*Based on Orsat analysis for CO₂ and O₂ only; other percentages calculated by O₂ and N₂ balances.

at Avg. Dense Bed Temp.

**Equilibrium constant for the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$. Figures are from McBride's Thesis, p. 189 (his data are from Austin and Day and from Rossini, et.al., for graphite).

FIGURE 4.

VARIATION OF TEMPERATURE IN THE LOWER REGION OF DENSE
DURING RUN NO. 7.



V. DISCUSSION OF RESULTS AND CONCLUSIONS.

A. Local Overheating.

Runs 1 through 5, at temperatures ranging from 1300-1900°F. and superficial gas velocities ranging 0.25-0.60 FPS, indicate that the tendency towards local overheating was sufficiently overcome by solids mixing to prevent hotspot formation under these operating conditions. The "Deviation of the Individual Thermocouples from the Average Dense Bed Temperature" in Runs 2 and 3 is biased on the low side due to the fact that the exposed thermocouples (hot junction only) were short-circuited to one another by the coke and the porcelain cement used to bind them together. This effect of diminishing the amount of temperature variation indicated is believed to have been small, however, because the electrical resistance between thermocouples was almost always several orders of magnitude higher than the resistance of the thermocouple wires, themselves.

Run 6 shows that the bottom 12-15 inches of the dense bed were essentially isothermal during the ^{run} except during the last thirty minutes, when the bottom couple climbed 10°F. above the next three. Ash agglomeration $\frac{1}{2}$ " thick found on the screen intimates that a hotspot (at least a mild one) had begun. The higher "Deviation" figures for Run 6 are apparently due to the fact that thermocouple #6 was not quite covered by the fluidized coke. This is quite possible, even though bed weight

and superficial velocity were essentially the same as those for Runs 2, 3, and 4, during which thermocouple #6 was at about the same temperature as those below it. Unknown effects have been found to alter the mechanical behavior of a fluidized bed operating under the same controlled conditions from day to day. (1)

Run 7, as recorded in Table 1 and Figure 4, pp. 15 and 18 respectively, clearly shows the formation of a mild hotspot (only 10^oF. above the rest of the dense bed, whereas Paxton's hotspots were usually 40^o hotter than the rest of the bed) at the bottom of the bed, its gradual dissipation and subsequent cooling. Even though the superficial gas velocity was about 0.65 FPS, the rate of heat release above 1900^oF. was too great for the solids mixing conditions that prevailed. The heavier formation of ash on the screen found after the run was similar in appearance to the formation found after Run 6. This bears out the writer's belief that a similar hotspot was in the making at the time Run 6 was ended. The fact that the operating conditions were at about the same temperatures during the two runs, but that the superficial velocity was 0.3 FPS in Run 6 and 0.65 FPS in Run 7, would indicate, also, that a hotspot likely did begin in Run 6, which had poorer solids mixing due to the lower superficial velocity.

Figure 4 shows that the portion of the dense bed above the burnt-out hotspot (now cooling to temperatures

far below the rest of the bed) held a fairly steady pattern with respect to the average temperature of this portion of the bed, as long as the run continued. Thus, the hot-spot did not travel up the bed (as Paxton's hotspots did occasionally) although it easily might have - in the author's opinion - if the run had been allowed to continue longer, due to the channeling of the inlet gas through the ash agglomeration and resultant poorer solids mixing directly above this agglomeration.

The writer concludes that no appreciable local overheating occurs in a fluidized coke bed using air at 0.3-0.6 FPS superficial gas velocity between 1300-1900^oF. under the other operating conditions that existed during his runs. Above 1900^oF., however, slight overheating is to be expected for the inlet region design and other conditions employed. This mild overheating problem might be eliminated entirely by another inlet region design that affords better solids mixing at the bottom of the bed.

B. Increase in Average Bed Temperature vs. Time.

Figure 3, p.16, compares the temperature rise of the average dense bed temperature during the seven runs, illustrating the more rapid climb at higher superficial gas velocities. This would be expected, since gas analysis of the exit stream always indicated essentially total O₂ consumption; consequently, higher superficial velocity, corresponding to greater mols/minute of O₂ consumed, would release heat of combustion at a faster rate within the bed.

The rate of temperature climb would be expected to diminish at higher temperatures due to increased O_2 consumption to form CO ($C + O_2 = CO_2$, $\Delta H_{60^\circ F.} = -170,500$ Btu/lb.mol O_2 ; $2C + O_2 = 2CO$, $\Delta H_{60^\circ F.} = -96,000$ Btu/lb.mol O_2) and due to greater rate of heat loss from the hot reactor to its surroundings (the latter effect would be quite small because heat transfer from the hot reactor was controlled by the rate of heat conduction through the "Santocel" lagging). These effects are not discernible in Figure 3. A plot of "Equilibrium" Heat Loss to Surroundings vs. Average Dense Bed Temperature (as measured by thermocouples in the dense bed immediately before starting or terminating a run) is given in Figure 5, p.23. This plot shows that the effect of higher temperatures on the rate of heat loss is, in fact, small, as expected - at least, it is within the errors inherent in calculating the "Equilibrium" Heat Loss. (See Appendix, "B", for a sample calculation of "Equilibrium" Heat Loss to Surroundings, p.28).

C. Comparison of the Author's Data with McBride's Data for O_2 - N_2 Mixtures.

Table 3, p.24, compares the author's data with McBride's data for O_2 - N_2 mixtures. The results do not agree, apparently mainly due to the greater weight of coke bed and the lower O_2 partial pressure used in McBride's runs.

McBride illustrated in his thesis that the CO pro-

FIGURE 5

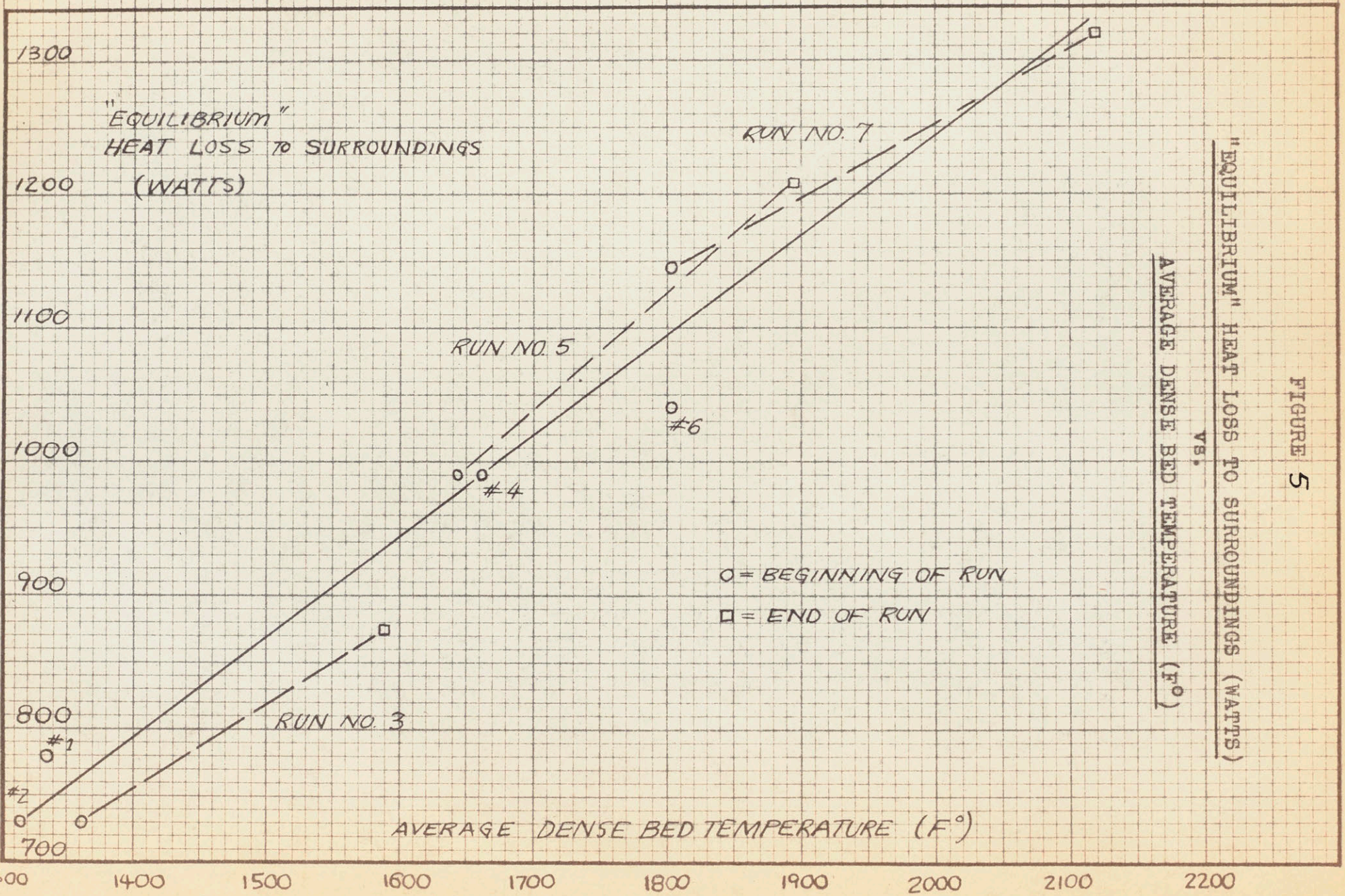


TABLE 3.

COMPARISON OF WEIDMAN'S DATA WITH MCBRIDE'S DATA

FOR O₂-N₂ MIXTURES

Run No.	Avg. Dense Bed Temp. (F°)	Superficial Vel. (FPS)	Carbon in Bed (lb. atoms)	Total C Gasification Rate (lb. atoms min. x 10 ⁴)	Fraction Total C Gasified per min. x 10 ⁴	CO Production Rate (lb. mols min. x 10 ⁴)	Fraction C Gasified as CO per min. x 10 ⁴	Exit Gas Ratio $\frac{P(\text{CO})^2}{P(\text{CO}_2)}$	
Weidman's Data	3	1589	0.30	0.081	0.67	8.33	0.26	3.22	0.0607
	5	1893	0.61	0.072	1.53	21.3	1.14	15.9	0.63
	7	2118	0.68	0.059	1.91	32.5			
McBride's Data	1600	0.77	0.207	1.24	5.98	0.228	1.159		0.0092
	1600	0.79	0.208	1.24	5.94	0.235	1.135		0.0101
	1900	0.80	0.210	1.89	9.0	1.77	8.43		4.732
	1900	0.80	0.207	1.91	8.2	1.81	8.75		5.973

NOTE: There was negligible O₂ in the exit gas of both Weidman's and McBride's runs. Weidman's inlet gas was air. McBride's inlet gas was O₂ and N₂ mixed with ratio O₂:N₂ = 0.22. Weidman's total reactor pressure (bottom of bed) was 31 in. Hg.; McBride's was 33 in. Hg.

duction rate for the O_2-N_2 runs was practically the same as that for the CO_2-N_2 , which would indicate that the entering O_2 is converted to CO_2 immediately at the bottom of the bed, then is partially reduced to CO as it flows upward through the hot coke.

This hypothesis is upheld by the author's finding that mild local overheating occurs only above $1900^{\circ}F.$; this local overheating occurs at the bottom of the bed, at least, in the beginning stages. This would not be expected if CO_2 and CO were primary products only, because the increasing equilibrium favor to the formation of CO at higher temperatures would correspondingly reduce the rate of heat release.

VI. RECOMMENDATIONS.

Solids mixing at the inlet region is the main problem to be overcome in order to eliminate mild hotspots in a coke bed fluidized in air above 1900^oF. in a commercial size reactor, assuming that the rest of the bed will mix as well as the author's 2"dia. x 18" dp. bed. More design work and experimentation on the inlet region, to improve solids mixing there, is desirable before building a large reactor.

APPENDIX

A. Details of Apparatus and Procedure.

The thermocouples used were 20 gage Chromel and Alumel, fused at the hot junction in an oxy-acetylene flame using a fluorspar flux. The thermocouples used were not calibrated, since relative temperature variation, rather than a precise measurement of the level of temperature in the bed, was desired. Runs 1 and 2 used thermocouples made from the same spools of Chromel and Alumel wire; Run 3 employed couples made from two different spools; Runs 4 through 7 used the same identical thermocouples, made from the second pair of spools. Experience has shown that it is not necessary to calibrate all couples made from the same pair of spools, except for the most exacting work. In this case, any difference of properties affecting the indicated temperature of thermocouples made from two different pairs of spools was not noticeable.

Two capillary gages were calibrated at room temperature (75°F.) by means of a wet-test meter, timer and compressed gas (N₂ was used with one; air was used with the other). The data points were correlated according to $\frac{100q}{\sqrt{P}}$ vs. ΔP where

q = gas flow rate at 1 atm. and 75°F. (cu. ft.
B.D. air/min.)

P = pressure immediately downstream from capillary (in. of Hg. abs.)

ΔP = pressure drop across capillary (in. of Hg.)

See Figures 6 and 7, pp. 29 and 30, for the calibration curves of the two capillary gages.

Gas samples were collected over mercury and analyzed according to standard Orsat technique by a professional analyst.

B. Sample Calculations.

The ratio $k_p = \frac{(P_{CO})^2}{P_{CO_2}}$ for the reaction $CO_2 + C = 2CO$ was calculated as follows:

Using the Exit Gas Analysis figures from the third gas sample of Run 3 (See Table 2, p. 17), which are

CO ₂	15.12%
CO	9.58
O ₂	0.00
N ₂	<u>75.30</u>
	100.00%

$$k_p = \frac{(0.0958 \times 1 \text{ atm.})^2}{(0.1512 \times 1 \text{ atm.})} = 0.0603$$

"Equilibrium" Heat Loss to Surroundings was calculated as follows:

An energy balance on the reactor during operation at near-thermal equilibrium gives

$$\left[(\text{Electrical Energy Input}) + \Delta H_{C+O_2=CO_2} + \Delta H_{2C+O_2=2CO} \right] =$$

$$\left[(\text{"Equilibrium" Heat Loss to Surroundings}) + (\text{Enthalpy of Exit Gas}) \right] \text{ above } 75^\circ\text{F. base temp.}$$

FIGURE 6

CALIBRATION CURVE FOR AIR CAPILLARY GAGE.

q = Air flow rate at 1.0 atm. & 75°F.
(cu. ft. B.D. air/ min.)

P = Pressure immediately downstream from capillary
(in. of Hg. abs.)

ΔP = Pressure drop across capillary
(in. of Hg.)

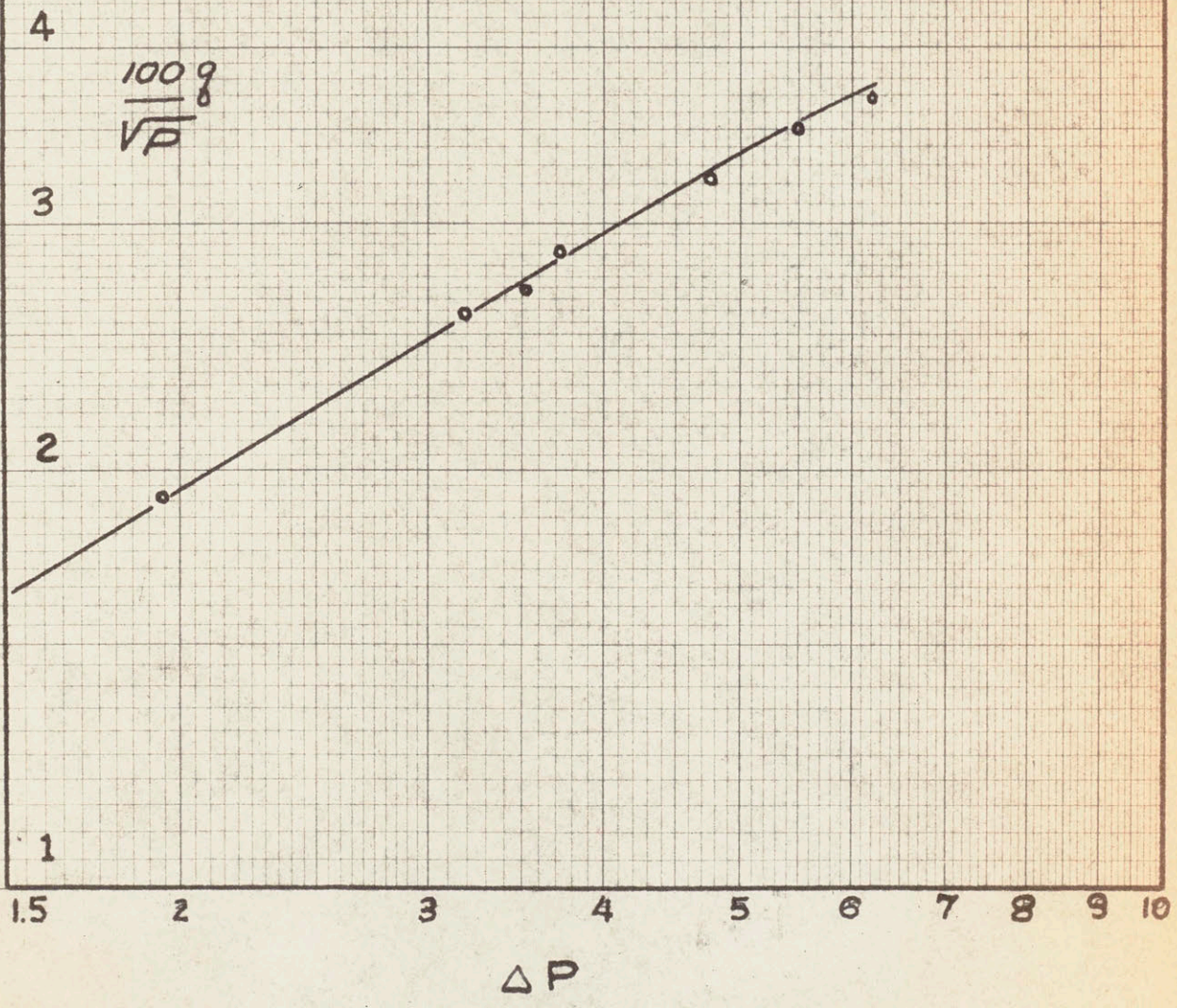


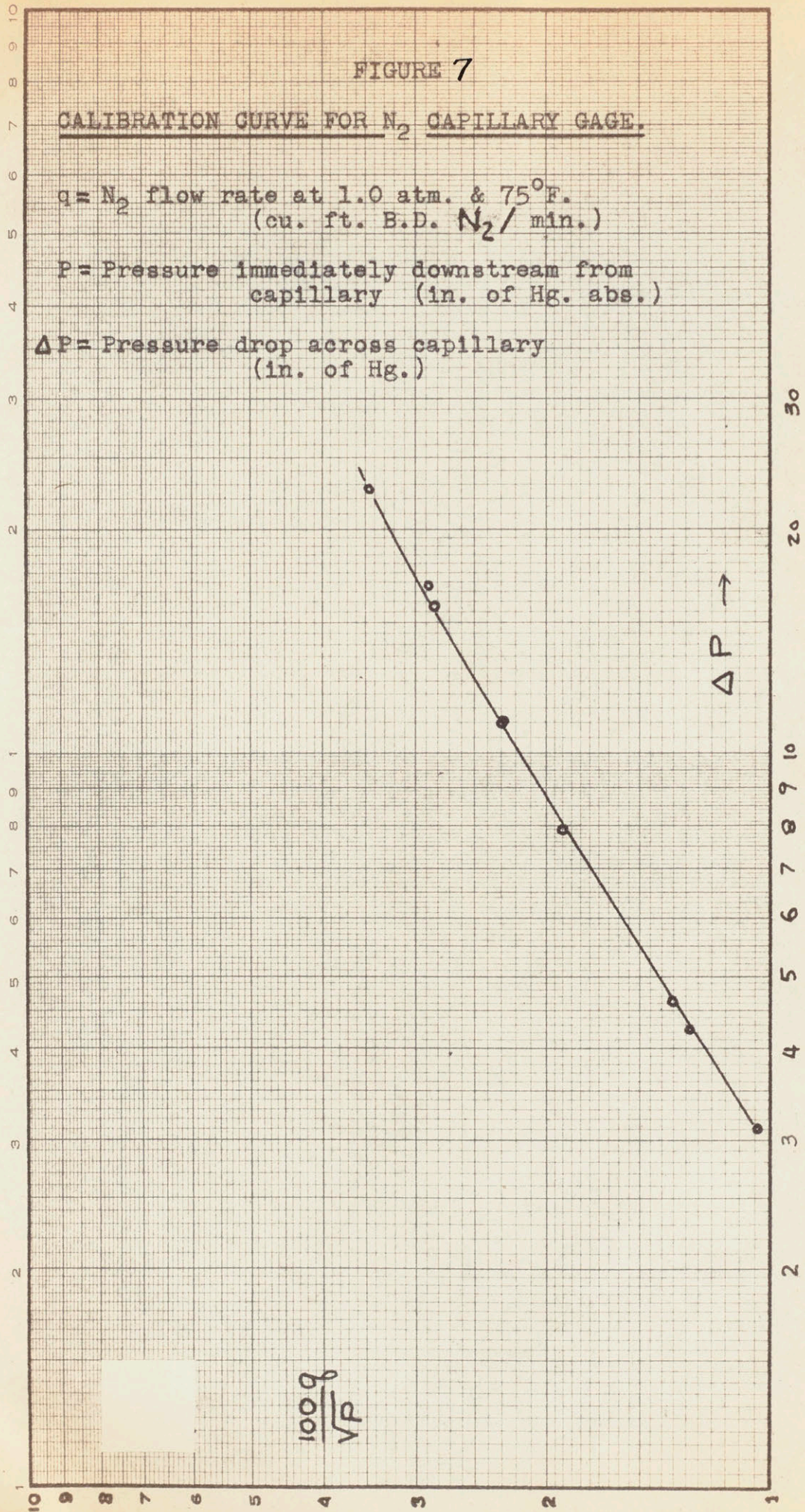
FIGURE 7

CALIBRATION CURVE FOR N₂ CAPILLARY GAGE.

q = N₂ flow rate at 1.0 atm. & 75° F.
(cu. ft. B.D. N₂ / min.)

P = Pressure immediately downstream from
capillary (in. of Hg. abs.)

ΔP = Pressure drop across capillary
(in. of Hg.)



For illustration, consider the operating conditions of Run 3 at the time of the third gas sample.

Electrical Energy Input = 730 watts
(Table 1, p. 15)

Avg. Dense Bed Temperature = 1589°F.

Superficial Gas Velocity = 0.30 FPS (corresponds to an O₂ feed rate of 0.67x10⁻⁴ lb.mols./min.)

Temperature of Exit Gas = about 160°F. (at the top of the reactor-estimated by touch)

Composition of Exit Gas = Same as above.

Calculating,

$$\Delta H_{C+O_2=CO_2} = 0.67 \times 10^{-4} \frac{\text{lb.mols. O}_2 \text{ consumed}}{\text{min.}}$$

$$\times \frac{15.12 \text{ lb.mols. CO}_2 \text{ formed}}{24.70 \text{ lb.mols. O}_2 \text{ consumed}}$$

$$\times \frac{170,500 \text{ Btu released}}{\text{lb.mols. CO}_2 \text{ formed}}$$

= 7.00 Btu. released/min. = 123 watts.

Similarly,

$\Delta H_{2C+O_2=2CO} = 22 \text{ watts}$

The Enthalpy of the Exit Gas is negligible since the average heat capacity of CO and N₂ is 8.27 Btu/lb.mol.F° and that of CO₂ is 11.1 Btu/lb.mol.F° in this temperature range and the magnitude of the flow rate is quite low.

Therefore,

["Equilibrium" Heat Loss] =

$$\left[(\text{Electrical Energy Input}) + \Delta H_{\text{C} + \text{O}_2 = \text{CO}_2} + \Delta H_{\text{2C} + \text{O} = \text{2CO}} \right]$$

$$= 730 + 123 + 22 = 875 \text{ watts lost to surroundings}$$

when avg. dense bed temp. is 1589°F.

C. Discussion of Errors.

1. Temperature measurement: As mentioned above under Appendix "A," the error of the relative temperature indications of the different thermocouples due to variation of the physical properties of the thermocouples used is believed to be negligible. The main error of relative temperature measurement stems from the inaccuracy of the potentiometer used (read to the nearest 0.1 millivolt, which corresponds to 4.5-5.0°F.) and observational errors involved in reading the temperature from a plot of temperature vs. millivolts output for Chromel-Alumel thermocouples. The overall average error is estimated at $\pm 3^\circ\text{F}$.

The error in the absolute values of temperatures recorded is unknown, but $\pm 25^\circ\text{F}$. is considered a reasonable estimate of this error.

2. Superficial gas velocity: Errors in measuring superficial gas velocity originate mainly from errors of capillary gage calibration and observational errors in meas-

uring the height of mercury indicating the pressure drop across the capillary gage. The latter source of error was more important. In addition to these errors of measurement, the flow rate, itself, varied between measurements; therefore, the measured flow rates are average values. The combined error in superficial velocity is estimated at $\pm 5\%$.

3. Electrical Energy Input: The error in calculating the electrical energy input is estimated from the plot of "Equilibrium" Heat Loss to Surroundings vs. Avg. Dense Bed Temperature (see Figure 5, p.23). Greatest deviation from the estimated line of best fit occurs at 1800°F . and is equal to about ± 50 watts.

4. Exit gas analysis: The figures on exit gas composition are based on Orsat analysis for CO_2 only, although, O_2 and, occasionally, CO were analyzed. The percent in this method would be expected to be greatest in the second sample of Run 7, where CO_2 content was at a minimum (see Table 2, p.17). This sample was analyzed for CO_2 , O_2 and N_2 ; the value of CO calculated from the CO_2 content agreed with the value of CO obtained by analysis within 5%. This is likely the maximum error in the CO per centages recorded. The average error in the CO_2 and CO percentages is probably $\pm 2\%$.

D. Location of the Original Data.

The original data is in the hands of Dr. E.R. Gilliland, Thesis Supervisor.

E. Literature Citations.

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