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SUBJECT: Oxygen and Temperature Profiles in Charcoal Beds Near the Charcoal Ignition Temperature

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ABSTRACT

A study of ignition of charcoal in shallow beds was made in relation to oxygen and temperature profiles in the beds. The results indicate that depletion of oxygen is not great in the charcoal beds until after ignition has occurred. Since the ignition temperature is not observed to be a strong function of oxygen concentration over the ranges encountered, it is concluded that ignition will first occur in the hottest portion of a shallow charcoal bed. This was confirmed experimentally.

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1. SUMMARY

Ignition of charcoal in shallow beds was studied in relation to oxygen and temperature profiles in the beds. The results indicate that depletion of oxygen is not great in a shallow charcoal bed until after ignition has occurred. With air flowing over the coarcoal, the oxygen concentration did not fall below 17 mole % before ignition, while after ignition, depletion of oxygen down to 1 mole % was observed. Before ignition, an increase in temperature with distance into the bed was observed, and this temperature increase was attributed to heat generation due to slow oxidation of the carbon and to exothermic chemisorption of oxygen on the charcoal. Since the ignition temperature is not a strong function of oxygen concentration between 10 and 20 mole %, it was concluded that ignition will occur at the hottest portion of a shallow charcoal bed. This was confirmed experimentally. Finally, it was observed that ignition could take place in beds which were at temperatures below the normal ignition temperature by changing abruptly from nitrogen flow to air flow. This result indicates that if for some reason oxygen is depleted from the bed region, ignition can occur at a relatively low temperature when air is readmitted to the bed. This phenomenon was attributed to the formation of hot spots which exceeded the ignition temperature, due to the rapid exothermic chemisorption of oxygen on the oxygen depleted charcoal.

2. INTRODUCTION

In the event of an accident in a nuclear reactor, fission products could be released into the air within the reactor containment vessel, which is often the building housing the reactor. Among the fission products trapped within the containment vessel would be radioactive isotopes of iodine. Charcoal adsorbers are commonly used to remove this iodine from the containment air. Since the radioactive iodine adsorbed on the charcoal would produce heat upon decaying, the temperature of the charcoal could approach the ignition temperature under certain circumstances. For this reason, charcoal ignition is being studied as part of the Nuclear Safety Program at the Oak Ridge National Laboratory.

In-pile experiments on charcoal ignition make up part of the program. In these experiments, accident conditions are simulated by using short-lived isotopes of iodine to produce decay heat in the coarcoal. Out-of-pile experiments are being used to study ignition of charcoal in relation to a number of variables, such as air velocity, type of charcoal, and humidity.

As part of the out-of-pile program, we have studied charcoal ignition in relation to oxygen and temperature profiles in charcoal beds.

In previous studies of charcoal ignition, temperature and oxygen mole fraction gradients had existed within the bed before and at the time of ignition. Since the recording thermocouples were not necessarily placed

at the point of ignition and since oxygen profiles had not been obtained, the conditions at the point of ignition had not been clearly defined. The object of collecting temperature and oxygen profiles was to define these conditions.

In the course of this study, a workable technique for obtaining gas samples from within the charcoal bed was developed. Gas samples were taken at various depths in the bed prior to and after ignition. Thermocouple readings were recorded continuously so that temperature profiles were obtained in addition to the gas composition profiles. From these data, heat effects due to oxidation before ignition were calculated, and the locations of the ignition zones were compared to the profiles obtained.

3. PROCEDURE

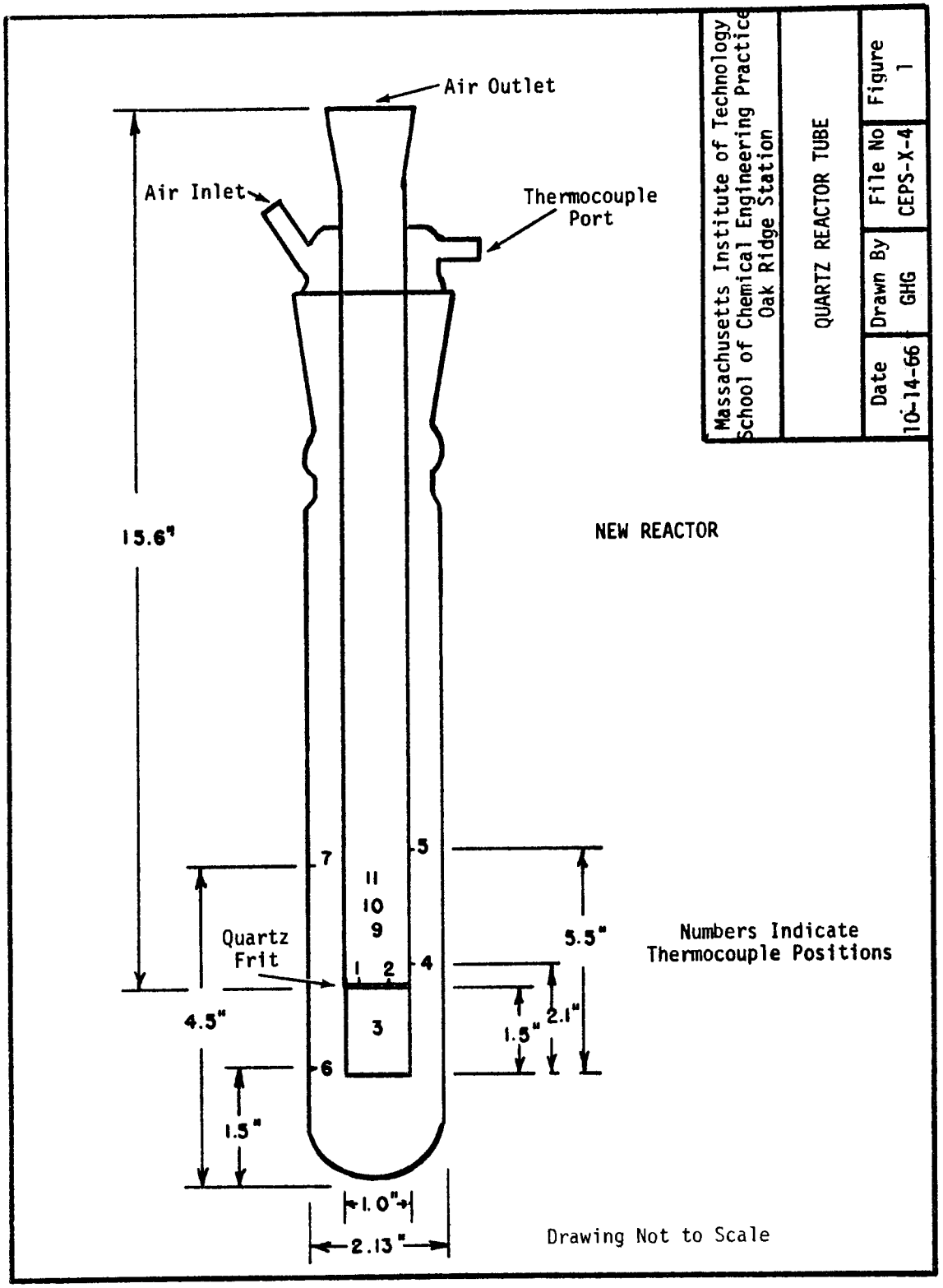
This section is divided into three areas of interest. First a description of the apparatus used for the ignition studies is presented, followed by the oxygen sampling technique, and concluded with the experimental procedure.

3.1 Experimental Apparatus

Two quartz reactors were used in this investigation. The second, referred to as the "new reactor" is depicted in Fig. 1 and differs slightly from the first reactor (referred to as the "old reactor"). A cylindrical electric furnace was provided for each reactor, with the new furnace being deeper than the old one. The reactors were designed so that air was heated as it flowed down through the annulus of the reactor. The heated air then flowed up the center tube through the charcoal bed which was supported on a frit. Thermocouples monitored the temperatures at the various locations noted on Fig. 1. The specific differences in the design of the two reactors were their size and their charcoal bed support. The old reactor was smaller, with an inner tube diameter of two-thirds of an inch compared with one inch for the new reactor. The charcoal support was a stainless steel screen in the old reactor while it was a quartz frit in the new reactor. Finally, the reactors differed in the number of thermocouples in them. The old reactor only had four thermocouples - one fixed to the screen, one at the bottom of the center tube, and two in the charcoal bed. The new reactor had ten thermocouples which were placed as shown in Fig. 1. Chart recorders were used to keep a continuous record of the thermocouple temperature.

3.2 Gas Sampling Apparatus and Technique

The sampling tubes and the sampling apparatus are illustrated in Fig. 2. The sampling tubes were designed as a part of this project to obtain concentration profile data. The sampling tubes, made of Pyrex glass, consisted of a 40-cm long capillary, a tapered end, and a sample bulb of about 0.5 cc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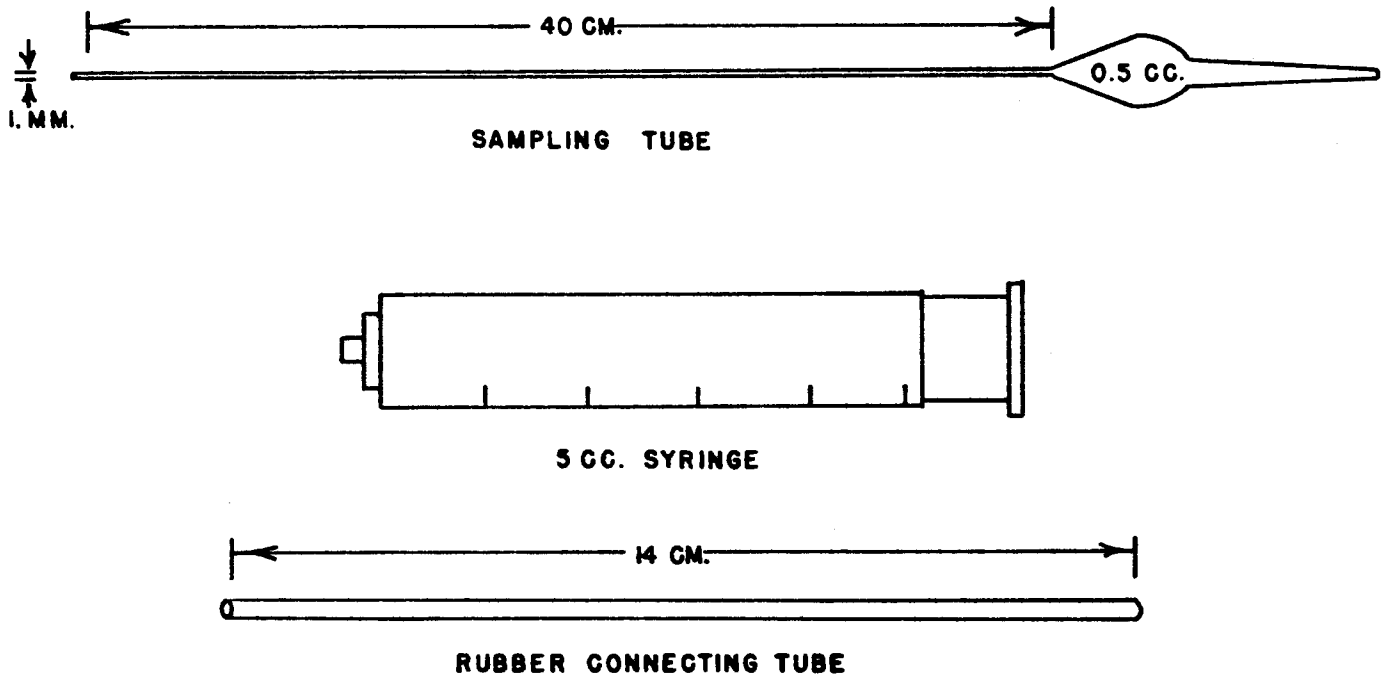
QUARTZ REACTOR TUBE
Figure 1
File No CEPS-X-4
Drawn By GHG
Date 10-14-66
Air Outlet
Air Inlet
Thermocouple Port
15.6"
NEW REACTOR
7
5
11
10
9
Quartz Frit
1
2
4
3
6
5.5"
Numbers Indicate Thermocouple Positions
4.5"
1.5"
2.1"
1.5"
1.0"
2.13"
Drawing Not to Scale



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GAS SAMPLING APPARATUS			
Date 10-14-66	Drawn By GHG	File No. CEPS-X-4	Figure 2

volume. Gas samples were collected by inserting the capillary into the charcoal bed while a glass syringe was attached to the other end with rubber tubing. Three to five cc of gas were withdrawn by means of the syringe, and the capillary was then sealed with a torch. The gas samples were sent to the Analytical Chemistry Division and analyzed for oxygen, methane, carbon monoxide, carbon dioxide, and nitrogen on a molecular sieve column in a gas chromatograph.

Two blank runs (see Appendix, Section 8.2), collected from a bed of glass beads through which nitrogen was passing, indicated that there was 10% air left in the bulb after a 3-cc flush with nitrogen. This difficulty, which results in oxygen analyses up to 2% too high, was overcome in later runs by flushing the sampling tube thoroughly with helium before a gas sample was collected. Residual helium did not affect the analytical results. The sample bulb volume was also reduced to about 1/3 cc and 5 cc of sample drawn through it instead of three.

Another 1% bias in the reported oxygen concentrations was introduced by the chromatographic analysis which lumped the argon and oxygen content of the air together as the oxygen concentration (see Section 8.2).

3.3 Experimental Procedure

The reactor startup procedure was as follows:

1) A charcoal sample of 5 gm was weighed out for the old reactor, or 8 gm for the new reactor.

2) The thermocouple leads were connected to the recorders.

3) The gas supply, either air or nitrogen, was turned on.

4) The rotameter was adjusted to obtain a flow of 1400 cc/min in the old reactor or 3100 cc/min in the new reactor. (These flow rates represent a linear velocity through the charcoal bed of 2708 cm/min in the old reactor and 2780 cm/min in the new reactor for a void fraction of 0.46 and at 623°K and 1 atmospheric pressure.)

5) The recorders were started.

6) The furnace was turned on.

The reactor was usually heated rapidly to a bed temperature of about 275°C. At this temperature, the heating rate was slowed down. The ignition temperature was approached at various heating rates between 0.03 °C/min and 20 °C/min during different runs. Heating rates were somewhat difficult to reproduce because of time lags between the furnace and its controller. This was due to the large heat capacity of the furnace. In some cases, the charcoal bed was heating even after power to the furnace had been cut back. After an ignition, the air supply and furnace were turned off to allow the charcoal to cool. When the bed had cooled, air flow was again started and another experiment was begun.

Prior to taking a gas sample, a sampling tube was prepared by flushing it with helium. The tube was then inserted to a predetermined depth into the charcoal bed, and a sample was drawn.

4. RESULTS

4.1 Steady State Temperature Profiles with Nitrogen Flow

It was discovered early in the program that an isothermal bed of charcoal could not be achieved in the old reactor at steady state even with nitrogen flowing through the reactor instead of air. The same was true of a bed of glass beads. Data for two steady states with glass beads and one steady state with charcoal and nitrogen appear in Table 1. About 2.5 hr were required to achieve steady state. On another occasion, temperatures were measured just outside the outer tube wall of the reactor at various depths in the furnace on opposite sides of the tube. These data appear in Table 2.

Table 1. Steady State Temperature Profiles with Nitrogen Flow Through the Old Reactor

Thermocouple Position	Temperature, °C		
	Glass Bead Bed		Charcoal Bed
	Profile 1	Profile 2	
Gas Inlet	283	370	374
Screen	302	398	401
Lower Bed	308	401	406
Upper Bed	296	387	393

Table 2. Temperatures Inside Old Furnace

Distance Down from Top (cm)	Temperature, °C	
	Side 1	Side 2
6.0	340	350
12.1	390	410
18.6	335	360
20.7	285	300

Steady state temperature profiles with nitrogen flow in the new apparatus showed that, unlike the old apparatus, the new apparatus heated up evenly. As shown in Table 3, thermocouples 1, 2, 3, 9, 10, and 11 did not disagree by more than five degrees in any case. In Fig. 3 the temperatures are plotted against height in the bed, and an essentially flat profile is obtained. The total height of the bed was 3.2 cm.

Table 3. Steady State Temperatures for a Charcoal Bed With Nitrogen Flow in the New Apparatus

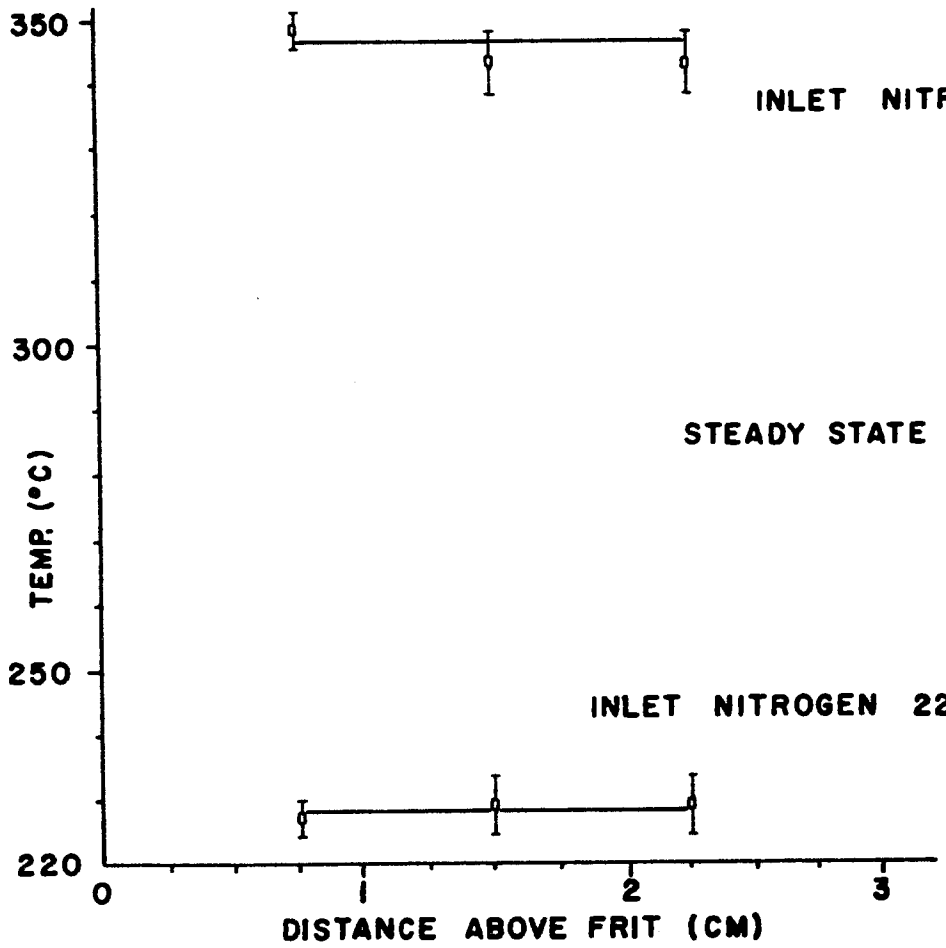
Thermocouple No.	Distance Above Frit (cm)	Temperatures at Steady State, °C		
		Profile 1	Profile 2	Profile 3
3 (inlet gas)	-	339	343	225
1 (frit)	0	340	345	226
2 (frit)	0	338	343	225
9 (lower bed)	0.76	343	348	227
10 (middle bed)	1.52	343	347	229
11 (upper bed)	2.28	343	347	229

4.2 Oxygen Concentration Profiles

In the old reactor, five air samples were taken at various positions in a charcoal bed at a nearly steady state condition during which the maximum rate of temperature change was 1 °C/min. The mole fraction of oxygen in each of these samples is plotted against the height in the bed at which it was taken in Fig. 4 as the 300°C profile. The sample with the greatest depletion of oxygen showed 18.7% oxygen. However, as the sample tubes used for the series of runs in the old reactor were not flushed with helium, the reported oxygen analyses could be too high by as much as 3% (see Section 8.2). The temperature levels at which these samples were taken are presented in Table 4.

Table 4. Temperatures for 300°C Oxygen Profile

Air inlet to inner tube	270 to 278°C
Screen support for bed	287 to 295°C
Lower portion of bed	299 to 305°C
Upper portion of bed	290 to 300°C



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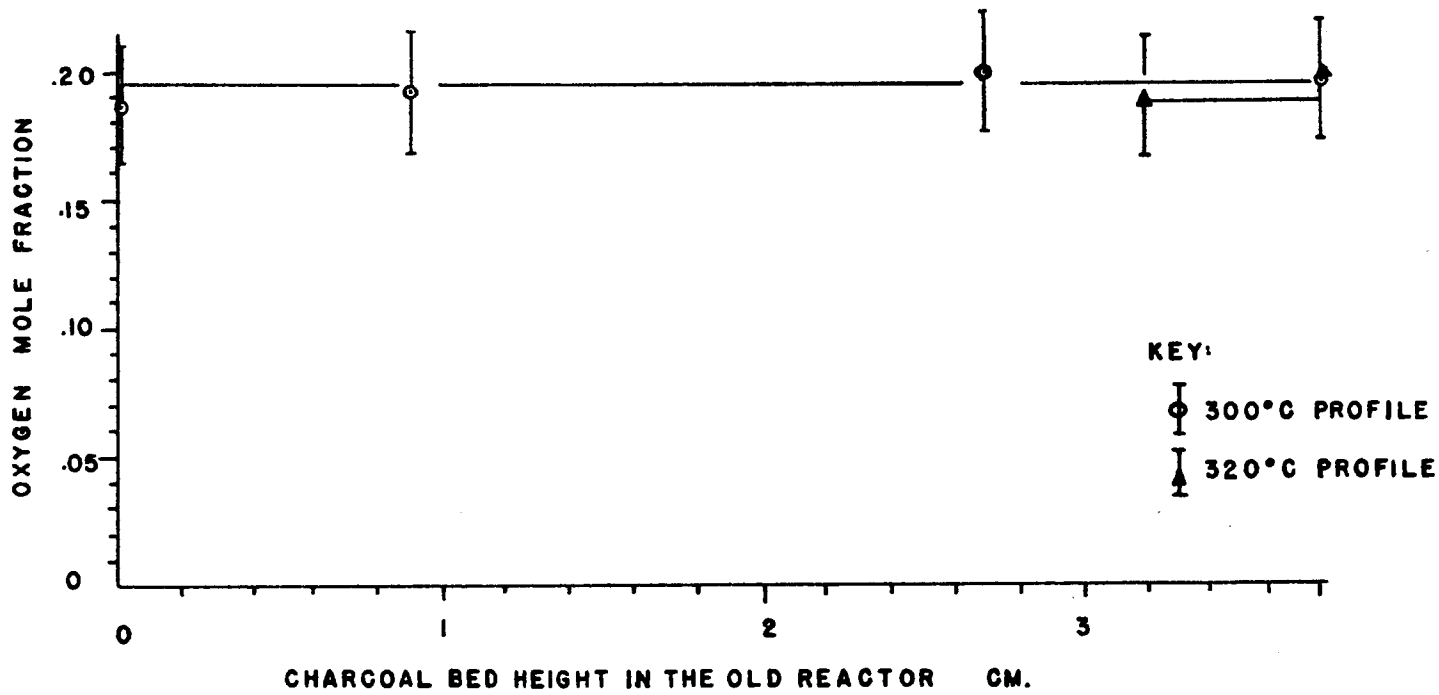
NITROGEN-CHARCOAL TEMPERATURE PROFILES
IN NEW REACTOR

DATE	DRAWN BY	FILE NO.	FIG.
10-14-66	GHG	CEPS-X-4	3



Massachusetts Institute of Technology School of Chemical Engineering Practice Oak Ridge Station			
CONCENTRATION PROFILES IN OLD REACTOR			
Date 10-14-66	Drawn By GHG	File No. CEPS-X-4	Figure 4

The air analyses for these samples are tabulated in Table A-1 in the Appendix. Two samples were also taken in the old reactor at bed temperatures between 320 and 323°C with the maximum rate of change of temperature being 0.5 °C/min. These two points are labeled "320°C Profile" on Fig. 4. Analytical data appear in Table A-2 in the Appendix.

Using the new reactor, samples were taken at various bed depths. Five of these were again taken at fairly constant conditions with the bed temperatures noted in Table 5. The maximum rate of change of temperature in the bed for this experiment was 1 °C/min.

Table 5. Temperatures in the Bed for Fig. 5 Profile

Air inlet	290 to 296°C
Quartz frit	292 to 296°C
0.76-cm bed height	307 to 310°C
1.52-cm bed height	315 to 317°C
2.28-cm bed height	320 to 324°C

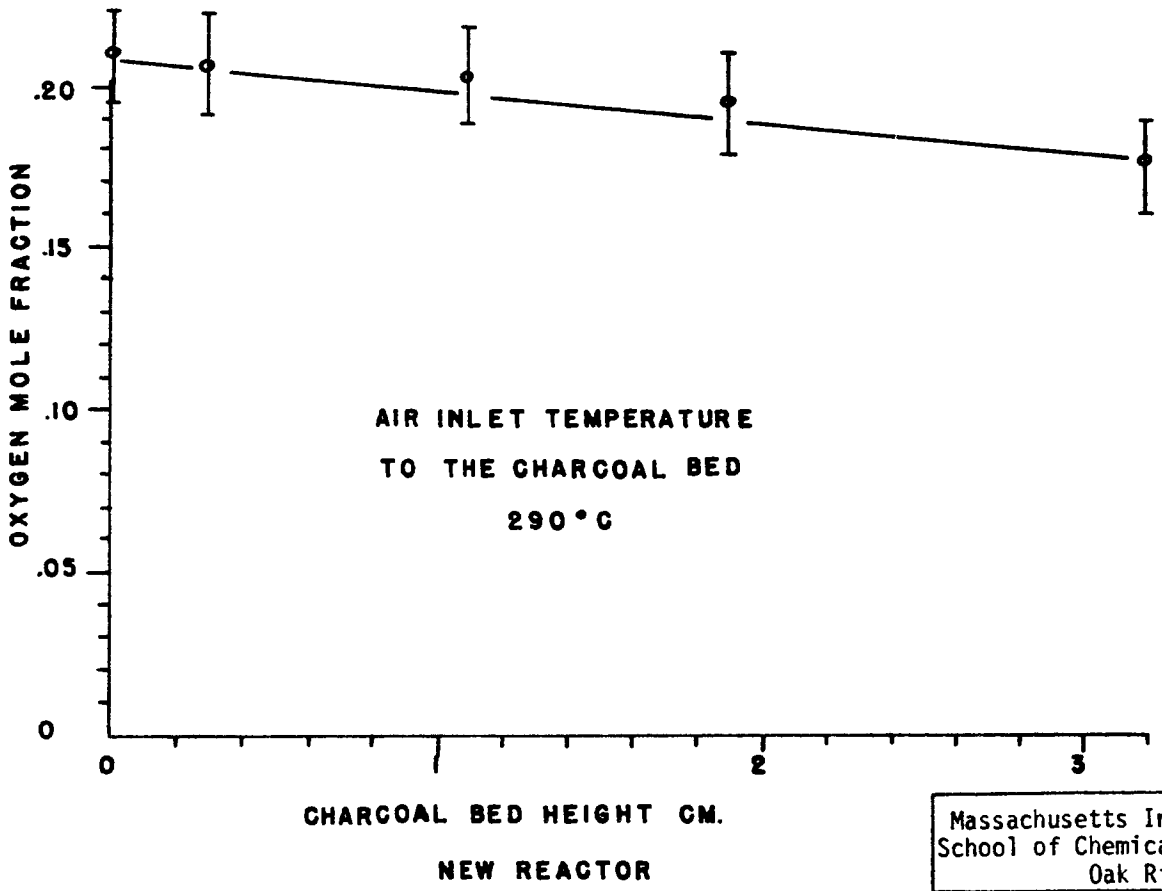
The oxygen profile obtained at these temperatures is presented in Fig. 5. Additional data appear in the Appendix, Section 8.1.

Since none of these samples showed an oxygen concentration below 17%, attempts were made to take samples closer to the time of ignition. Of these, two were drawn less than one minute before ignition, three were being drawn when ignition occurred, and three were taken after ignition had occurred but before the air supply had been shut off. The gas analyses are presented in Table 6. Two other samples taken 6 min and 15 min before ignition showed oxygen concentration of 18.9% and 17.9% respectively.

Table 6. Analyses of Gas Samples Taken Within One Minute of or During Ignition

Time Taken	Bed Height	N_2 (%)	O_2* (%)	CO_2 (%)	CO (%)	Total (%)
Before ignition	exit	80.8	17.3	2.2	--	100.3
Before ignition	exit	80.4	20.3	1.2	--	101.9
During ignition	0.7 cm	85.5	12.0	6.4	2.8	106.7
During ignition	2.5 cm	77.6	1.3	11.5	15.8	106.2
During ignition	exit	80.6	15.1	4.5	0.5	100.7
After ignition	frit	73.1	3.1	8.9	14.7	99.8
After ignition	1.5 cm	73.6	2.5	13.3	11.4	100.8
After ignition	2.3 cm	70.8	1.7	19.8	8.8	101.1

*Oxygen concentrations about 1% too high (See Section 8.2).



Massachusetts Institute of Technology School of Chemical Engineering Practice Oak Ridge Station			
CONCENTRATION PROFILE IN NEW REACTOR			
Date 10-14-66	Drawn By GHG	File No. CEPS-X-4	Figure 5

Additional data, including temperature profiles at ignition, are presented in Table A-4 in the Appendix.

4.3 Steady State Temperature Profiles with Air Flow

Steady state temperature profiles were obtained at different temperature levels in the new reactor with air flowing through the charcoal. The data are plotted in Fig. 6 and are tabulated in Table 7. The height of the bed used was 3.2 cm.

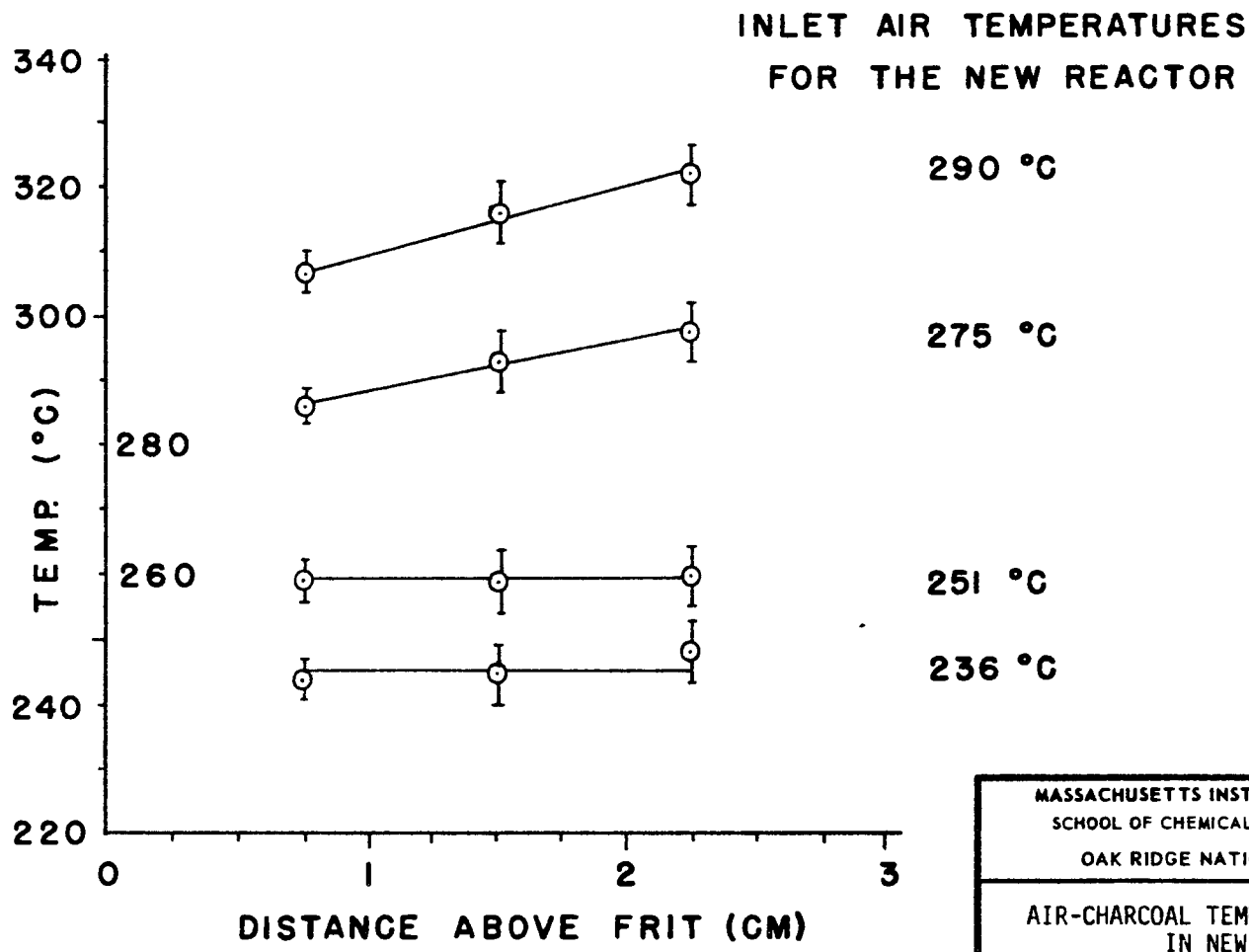
Table 7. Steady State Temperatures for a Charcoal Bed with Air Flow in the New Reactor

Thermocouple No. (See Fig. 1)	Height Above Frit (cm)	Temperatures at Various Steady States, °C				
		Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
3 (inlet air)	-	236	251	275	290	295
1 (frit)	0	239	255	271	295	300
2 (frit)	0	236	253	274	292	297
9 (bed)	0.76	244	259	286	307	327
10 (bed)	1.52	246	259	292	316	345
11 (bed)	2.28	248	260	298	322	350

4.4 Location of Ignition in Relation to Temperature Profiles

Eighteen ignitions were studied to determine which recording thermocouple indicated ignition first. Nine of these ignitions were run with the old apparatus.

In the runs with the old apparatus the upper and lower bed thermocouple temperatures were recorded on the same chart and the bed support temperature on a separate chart. The time lag between ignitions at various points in the bed was found to be between 10 and 20 sec. This time lag was just barely sufficient to allow a reliable judgement of which thermocouple had registered ignition first. The hottest thermocouples registered ignition first in eight of nine runs. Not much significance is placed in the run in which this did not happen because the temperature throughout the bed immediately before ignition did not vary by more than 10°C so that the bed was almost isothermal. A summary of the data collected with the old reactor is presented in Table 8. A more detailed summary is given in Table A-5 in the Appendix.



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AIR-CHARCOAL TEMPERATURE PROFILES
IN NEW REACTOR

DATE	DRAWN BY	FILE NO.	FIG.
10-14-66	S.T. Mayr	CEPS-X-4	6

Table 8. Location of First Ignition in Runs Made with the Old Apparatus

Date	Ignition No.	Thermocouple Registering Ignition First	Temperatures at Time of First Ignition (°C)				Hottest Point Ignited First
			Inlet Air	Screen	Lower Bed	Upper Bed	
9-28-66	1	Upper Bed	267	273	275	265	no
9-28-66	2	Lower Bed	-	-	310	308	yes
10-4-66	3	Upper Bed	265	280	320	370	yes
10-4-66	4	Upper Bed	295	318	345	352	yes
10-4-66	5	Lower Bed	277	293	325	307	yes
10-4-66	6	Lower Bed	272	286	305	288	yes
10-4-66	7	Lower Bed	298	313	330	314	yes
10-4-66	8	Lower Bed	282	297	310	292	yes
10-4-66	9	Lower Bed	291	315	337	323	yes

In the runs with the new apparatus the charts were speeded up 2-1/2 times to 1 in./min but not all the bed temperatures could be recorded on the same chart. In spite of the increase in chart speed, reliable judgements on the locations where ignition occurred first could not be made in this case, because the differences in times of ignition were found to be less than 10 sec. The low time lags, in comparison with the ones recorded with the old apparatus, are probably due to the more uniform heating of the charcoal bed in the new apparatus (see Section 4.1). The temperatures at which ignition occurred at the various points in the bed are tabulated in Table A-6 in the Appendix.

4.5 Effect of Oxygen Concentration on Ignition Temperatures

A few ignition runs were made with mixtures of air and nitrogen being fed to the reactor. The experimental results are presented in Table 9. The results seem to indicate that the ignition temperature is independent of the oxygen concentration of the inlet air down to about 5% oxygen. A 1% oxygen mixture did not cause ignition even at 490°C.

4.6 Changing from Nitrogen to Air Flow at High Temperatures

Three experiments were run with the new reactor in which nitrogen was run through the bed for at least 10 min. When the flow was abruptly changed from nitrogen to air in one of these runs, there was immediate ignition, with the three bed thermocouples reading between 310 and 312°C. In the other runs, a rise in the temperature was noted. In one case, the temperature rose from 278 to 292°C in about 1 min and then slowly decreased to 288°C. In the other case, the temperature rose from 298 to 320°C at which point ignition occurred. The data collected during this series of runs are summarized in Table 10.

5. DISCUSSION

5.1 Oxygen Depletions Before and After Ignition

From the data on oxygen concentrations presented in the Results, Section 4.2, the conclusion can be drawn that oxygen depletion is not great before ignition, but is almost complete after ignition. Even with samples taken no longer than one minute before ignition (in the new reactor) the oxygen concentration was found to be at least 17%. Just after ignition, however, the concentration dropped to between 1 and 3%. It should be noted that these numbers are probably too high by 1%. This is due to the fact that the chromatographic analysis included the 0.93% argon present in the air (11) in the oxygen analysis figure. (See Sections 3.2 and 8.2 which describe in detail the sampling and analytical techniques and the bias associated with them.)

Table 9. Effect of Oxygen Concentration on the Ignition Temperature

Inlet Gas Composition			Ignition Temperatures (°C)[a]		
% Air	% Oxygen	Point of First Ignition	T_{Hi}	T_{Av}	T_{Lo}
75	16	Upper bed	350	350	350
75	16	Upper bed	-	380[b]	-
50	10.5	Upper bed	385[b]	370[b]	350[b]
25	5	Upper bed	500[b]	357	343
5	1	No ignition at 490°C	-	-	-

[a]T_{Hi}, T_{Av}, and T_{Lo} are defined in Section 8.3 in the Appendix.

[b]Approximate values; ignition temperatures could only be read correct to 20°C from the recorder chart.

Table 10. Effect of Sudden Changes from Nitrogen to Air Flow on the Charcoal Bed Temperature

Run No.	Thermocouple No.[a]	Steady State Bed Temperatures with Nitrogen Flow (°C)	Bed Temperatures with Air Flow (°C)
1	9	278	291
	10	276	292
	11	275	294
2	9	298	Temperature rise followed by ignition at 320°C
	10	297	-
	11	296	Temperature rise followed by ignition at 325°C
3	9	312	Temperature rise followed by ignition at 313°C
	10	310	Immediate ignition
	11	310	Immediate ignition

[a]Thermocouple position in charcoal bed: No. 9 is 0.76 cm above frit; No. 10 is 1.52 cm above frit; No. 11 is 2.28 cm above frit.

5.2 Effect of Oxygen Concentration on Ignition Temperature

From the few results presented in Table 9, it seems that the ignition temperature is independent of the oxygen concentration of the inlet air down to about 5% oxygen (25% air in nitrogen). A 1% oxygen mixture did not cause ignition even though temperatures as high as 490°C were recorded in the bed. However, more ignition runs are needed to confirm the above observations before a more definite statement can be made.

5.3 Temperature Profiles at Steady State and Heat Effects Prior to Ignition

No conclusions could be made from the data obtained from the old reactor due to the uneven heating of the furnace. However, the new reactor was shown to heat evenly by achieving an isothermal bed at the same temperature as the inlet nitrogen flow (see Table 3 and Fig. 3). Thus the problem of uneven heating was eliminated. From this we concluded that any gradients in an air-charcoal run in the new reactor before ignition would be due to some sort of oxidation in the bed.

From Table 7 it can be noted that, in the investigated inlet air temperature range of 236 to 295°C, the bed becomes hotter than the inlet air and that the bed has a gradient in temperature (see Fig. 6). Heat must, therefore, be evolved in the bed prior to ignition and at temperatures considerably below the ignition temperature. This heat evolution has been calculated for each of the steady states listed in Table 7 by the method presented in Section 8.6 in the Appendix. In this method, the sensible heat gain of the air is calculated using temperatures taken at the air inlet (thermocouple 3) and high in the bed (thermocouple 11). This heat term is then equated to the total heat evolution in the bed by assuming that heat losses from the bed through the inner tube wall were small. By the method shown in Section 8.7 it was estimated that, for the case of the highest heat evolution of 50 cal/min, the corresponding heat losses were 9 cal/min. The best check on the validity of the negligible heat loss assumption is probably offered by calculating the rate of heat evolution based on the inlet and exit gas carbon dioxide compositions.

Small but significant amounts of carbon dioxide were noticed in many of the gas samples taken prior to ignition. The reaction

$$C + O_2 \longrightarrow CO_2$$

has a heat of reaction of 97 kcal/mole (8) when the carbon is present as charcoal. From this value and from the rate of carbon dioxide production, a separate estimate of the rate of heat evolution was obtained. From the data for samples OP-10-5-1 and OP-10-6-1 (see Tables A-3 and A-4 in the Appendix) estimates were made of the rate of heat evolution at inlet air temperatures of 290 and 295°C (see Section 8.8 in the Appendix for sample calculations). At 290°C, the rate of heat evolution was calculated to be 90 $\pm$ 9 cal/min, and at 295°C it was calculated to be 285 $\pm$ 30 cal/min. The

sensible heat gain calculations give estimates of 30 cal/min and 50 cal/min for the same temperatures.

At 290°C, one fifth of the oxygen depleted in the bed came off as carbon dioxide. Taking experimental error into account, at most, 47% of the oxygen came off as carbon dioxide. For the 295°C case, 60% of the oxygen depleted came off as carbon dioxide, but within experimental error, it is possible that all the oxygen depleted came off as carbon dioxide. Also for sample IR-0-2A-1 (see Table A-1 in the Appendix), there were fewer atoms of oxygen leaving the bed than there were entering, and this discrepancy cannot be attributed to experimental error. It would appear, then, that some of the oxygen is being adsorbed onto the charcoal, since not all of the oxygen depleted comes off as carbon dioxide or carbon monoxide. (There was no carbon monoxide in these samples.)

Taking the data of sample OP-10-6-1 as a basis of calculation along with the heat evolution calculated from the sensible heat gain of air of 50 cal/min, the heat of reaction is calculated as 7.9 kcal/mole. When the logarithm of the rate of heat evolution was plotted versus the reciprocal of the temperature, an energy of activation was calculated as 3 kcal/mole. Both of these unusually low values are an indication of physical adsorption. However, the carbon dioxide data indicate that the heat effects calculated from sensible heat data are low, and therefore the above heat of reaction and energy of activation are probably low. Also it seems unlikely that a continuous increase in physical adsorption would occur during our steady states since physical adsorption equilibrium is attained in about 5 min (1). On the other hand, chemisorption requires approximately 6 hr to attain equilibrium (1). The fact that not all the oxygen which is depleted comes off as carbon dioxide or carbon monoxide is probably due to chemisorption of that portion of the unreacted oxygen.

5.4 Effect on Bed Temperature of Sudden Changes from Nitrogen to Air Flow

It should be noted in relation to reactor safety with charcoal adsorbers that it was possible to cause a charcoal bed (in contact with nitrogen) at a temperature below the ignition temperature to suddenly ignite when the flow was abruptly switched from nitrogen to air. This is clearly shown by the results presented in Section 4.6 and summarized in Table 10. It is suggested that this is due to rapid adsorption of oxygen onto sites on the charcoal from which oxygen had been stripped by the nitrogen. Indeed if a situation were to arise in which air flow was completely stopped and the oxygen in the adsorber depleted (i.e., by slow oxidation), turning the air back on could cause a fire in the bed even though the bed was "below" the ignition temperature.

5.5 Location of Ignition in Relation to Temperature Profiles

The results on the location of ignition fail to support the contention that the hottest position in the charcoal bed does not ignite first. In the nine ignition runs made with the old apparatus, the hottest thermocouple

registered ignition first eight times, and in the one case in which this did not happen the bed was almost isothermal (see Table 8). From our oxygen profile data, it seems unlikely that the hottest portion of the bed would not ignite first. We found that a feed stream of 10.5% oxygen ignited the bed at 350°C which was not significantly higher than ignition temperatures obtained with pure air on the same day. These results are in agreement with those of Milham (13), who found no effect on ignition temperature down to 15.9% oxygen. None of our profiles show depletions before ignition below 17% oxygen anywhere in the bed, which indicates that there is ample oxygen available to cause ignition at the hottest portion of the bed wherever it may be.

We noted that the frit and the screen were always at lower temperatures near ignition than the charcoal was. This was most likely due to cooling of these supports by the incoming air which was cooler than the bed. Since the frit and screen did not act as heat sources, it was expected that they would read between the gas and charcoal temperatures and this is borne out by the data in Table 7. Finally, it was noted in the results that in five cases the frit or screen did not register ignition at all even though ignition had already taken place within the charcoal bed. It is therefore strongly recommended that frit temperatures not be reported as the ignition temperature.

5.6 Temperature Difference Between Charcoal and Air

In Section 8.9 in the Appendix, it is shown that, in the charcoal bed, the temperature difference between the charcoal particles and the air flowing between them is about one degree at most before ignition occurs. The implied assumption, made use of throughout this report, that the thermocouple monitored gas temperature is equal to the surrounding charcoal temperature, is thus valid.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1) Oxygen depletion is not great before ignition and only becomes so after ignition.

2) A sampling method for extracting gas samples from within the charcoal bed has been developed and is subject to less than 10% error.

3) Heat generation in the bed was calculated from the sensible heat increase of the air stream and from carbon dioxide data. The carbon dioxide data indicate a heat generation 3 to 5 times as great as that calculated from sensible heats. The carbon dioxide data probably provide the better estimate of the heat effects.

4) The results strongly indicate that the hottest portion of the bed will ignite first except when the bed is almost isothermal.

5) It is possible to cause a bed in equilibrium with an oxygen deficient atmosphere (e.g., nitrogen) at a temperature lower than the ignition temperature, to ignite suddenly by changing from nitrogen to air flow.

6) Lowering the concentration of oxygen in the feed stream from 21% to 15 and 10% did not seem to significantly change the ignition temperature.

6.2 Recommendations

1) We recommend that the frit temperature not be reported as the ignition temperature since it reads low due to cooling by the inlet air. Instead, we recommend recording temperatures in the bed as the ignition temperature.

2) If studies of location of first ignition are to be performed, times should be accurately measured to within one second, which will require chart speeds of at least 3 in./min.

7. ACKNOWLEDGEMENTS

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8. APPENDIX

8.1 Gas Analysis Data

The data for the 300°C profile of Fig. 4 are presented in Table A-1. The sampling tubes had not been flushed with helium when these samples were taken.

Table A-1. Analyses of Gas Samples Taken in Old Reactor

Sample No.	Distance Above Frit (cm)	N_2 (%)	O_2 (%)	CO_2 (%)	CO (%)	Total (%)
IR-0-2A-1	0	81.3	18.7	-	-	100.0
IR-0-2A-2	0.9	79.6	19.2	0.5	-	99.3
IR-0-2A-3	2.7	81.1	20.3	0.5	-	101.9
IR-0-2A-4	Exit	81.0	19.5	0.5	-	101.0
IR-0-2A-5	Exit	80.2	19.8	-	-	100.0

The data for the 320°C profile of Fig. 4 are presented in Table A-2. The sampling tubes had not been flushed with helium when these samples were taken.

Table A-2. Analysis of Gas Sample in Old Reactor

Sample No.	Distance Above Frit (cm)	N_2 (%)	O_2 (%)	CO_2 (%)	CO (%)	Total (%)
E-0-A	Exit	80.3	19.8	1.04	-	101.1
298-48-5	3.2	79.3	18.9	0.86	-	99.1

The data for samples referred to in Fig. 5 appear in Table A-3. The sampling tubes were flushed with helium before these samples were taken. The temperature profile which existed at the time of sampling is included with each gas analysis.

Table A-3. Gas Analyses with Temperature Profiles at Time of Sampling in New Reactor

Sample OP-10-5-1	Exit Gas									
Temperature °C	290	294	295	307	315	320	305	286	295	298
Thermocouple No.	3	2	1	9	10	11	4	5	6	7
17.5% O_2, 81.2% N_2, 0.7% CO_2, no CO or CH_4, 99.4% Total										
Sample OP-10-5-2	1.9 cm above the frit									
Temperature °C	290	292	295	307	317	324	305	285	300	300
Thermocouple No.	3	2	1	9	10	11	4	5	6	7
19.4% O_2, 81.2% N_2, 0.8% CO_2, no CO or CH_4, 101.4% Total										
Sample OP-10-5-3	at the frit									
Temperature °C	290	292	295	307	316	322	305	286	300	300
Thermocouple No.	3	2	1	9	10	11	4	5	6	7
20.9% O_2, 80.3% N_2, 0.7% CO_2, no CO or CH_4, 101.9% Total										
Sample OP-10-5-4	0.3 cm above the frit									
Temperature °C	291	294	296	310	316	320	305	286	301	301
Thermocouple No.	3	2	1	9	10	11	4	5	6	7
20.5% O_2, 80.3% N_2, 0.6% CO_2, no CO or CH_4, 101.4% Total										
Sample OP-10-5-5	1.1 cm above the frit									
Temperature °C	296	295	296	310	317	320	305	286	300	300
Thermocouple No.	3	2	1	9	10	11	4	5	6	7
20.2% O_2, 80.8% N_2, 0.6% CO_2, no CO or CH_4, 101.6% Total										

The data for gas samples referred to in Table 4 appear in Table A-4. The sampling tubes were flushed with helium before these samples were taken. The temperature profile which existed at the time of sampling is included with each gas analysis.

8.2 Bias Associated with Gas Sampling Technique and Chromatographic Analysis

In order to test the sampling procedure used to obtain the oxygen concentration data, samples were collected with nitrogen passing through a bed of glass beads. One of these samples showed 2.35% oxygen and 97.0% nitrogen while the other showed 1.77% oxygen and 98.0% nitrogen. There was thus about 10% contamination from the original air in the sampling tubes which meant that the oxygen concentrations obtained during the runs using the old reactor were about 2% too high.

This difficulty was overcome in the subsequent runs with the new reactor mainly by flushing the sampling tubes thoroughly with helium before a gas sample was collected.

Another bias was introduced by the chromatographic analysis which lumped the argon and oxygen content of the air together as the oxygen concentration. As air contains 0.93% by volume of argon (11), this bias resulted in reported oxygen analyses which were about 1% too high.

Table A-4. Gas Analyses in the New Reactor with Temperature Profiles at the Time of Sampling Prior To, During, and After Ignition

Sample OP-10-5-6 Exit gas during ignition

Temperature °C	310	307	312	335	347	347	325	300	325	317
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

15.1% O_2, 80.6% N_2, 4.5% CO_2, 0.5% CO, no CH_4, 100.7% Total

Sample OP-10-6-1 Exit gas 40 sec before ignition

Temperature °C	295	297	300	327	345	350	319	290	310	306
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

17.3% O_2, 80.8% N_2, 2.2% CO_2, no CO or CH_4, 100.3% Total

Sample OP-10-6-2 2.3 cm above the frit, after ignition

Temperature °C	295	297	302	332	360	370	319	290	310	306
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

1.7% O_2, 70.8% N_2, 19.8% CO_2, 8.8% CO, no CH_4, 101.1% Total

Sample OP-10-6-3 At the frit, 15 min before ignition

Temperature °C	293	296	297	316	316	315	307	289	301	301
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

17.9% O_2, 77.9% N_2, 0.77% CO_2, no CO or CH_4, 96.6% Total

Sample OP-10-6-4 1.5 cm above frit, 6 min before ignition

Temperature °C	299	301	307	334	336	334	317	293	320	308
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

18.9% O_2, 77.2% N_2, 1.3% CO_2, no CO or CH_4, 97.4% Total

Sample OP-10-6-5 0.7 cm above the frit during ignition

Temperature °C	305	312	314	350	355	355	326	299	310	315
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

12.0% O_2, 85.5% N_2, 6.4% CO_2, 2.8% CO, no CH_4, 106.7% Total

Sample OP-10-6-6 Exit less than 1 min before ignition

Temperature °C	294	302	299	345	340	330	307	289	296	297
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

20.3% O_2, 80.4% N_2, 1.2% CO_2, no CO or CH_4, 101.9% Total

Sample OP-10-6-7 1.5 cm up after ignition

Temperature °C	305	311	308	337	340	335	319	298	312	313
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

2.5% O_2, 73.6% N_2, 13.3% CO_2, 11.4% CO, no CH_4, 100.8% Total

Sample OP-10-6-8 Frit after ignition

Temperature °C	294	302	297	324	327	335	305	290	304	303
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

3.1% O_2, 73.1% N_2, 8.9% CO_2, 14.7% CO, no CH_4, 99.8% Total

Sample OP-10-6-10 2.5 cm above the frit during ignition

Temperature °C	297	300	297	325	325	315	303	291	301	305
Thermocouple No.	3	2	1	9	10	11	4	5	6	7

1.3% O_2, 77.6% N_2, 11.5% CO_2, 15.8% CO, no CH_4, 106.2% Total

The approximate total bias in the reported oxygen analyses is thus:

a) without helium flushing, reported values about 3% too high,

b) with helium flushing, reported values about 1% too high.

8.3 Definition of Ignition Temperature

Figure 7 shows a typical curve for a time-temperature record of an ignition run and exemplifies the anomaly associated with the definition of an ignition temperature. T_{Lo} is the point of departure from the linear heating rate and is caused by an increase of heat generation in the charcoal bed. T_{Hi} is the temperature at which the oxidation of the charcoal is truly self-sustaining. T_{Av} is a compromise between T_{Lo} and T_{Hi}.

For the recording of data, the definition of the ignition tempeature must be made explicit. In a safety program either T_{Lo} or T_{Av} could be reported as an ignition temperature to be certain of remaining on the low side of the ignition temperature. If one defines the ignition temperature as the point of self-sustaining oxidation, then T_{Hi} is a logical choice. Typically T_{Hi} is about ten or fifteen degrees above T_{Lo} but in an extreme case T_{Hi} may be ninety degrees higher.

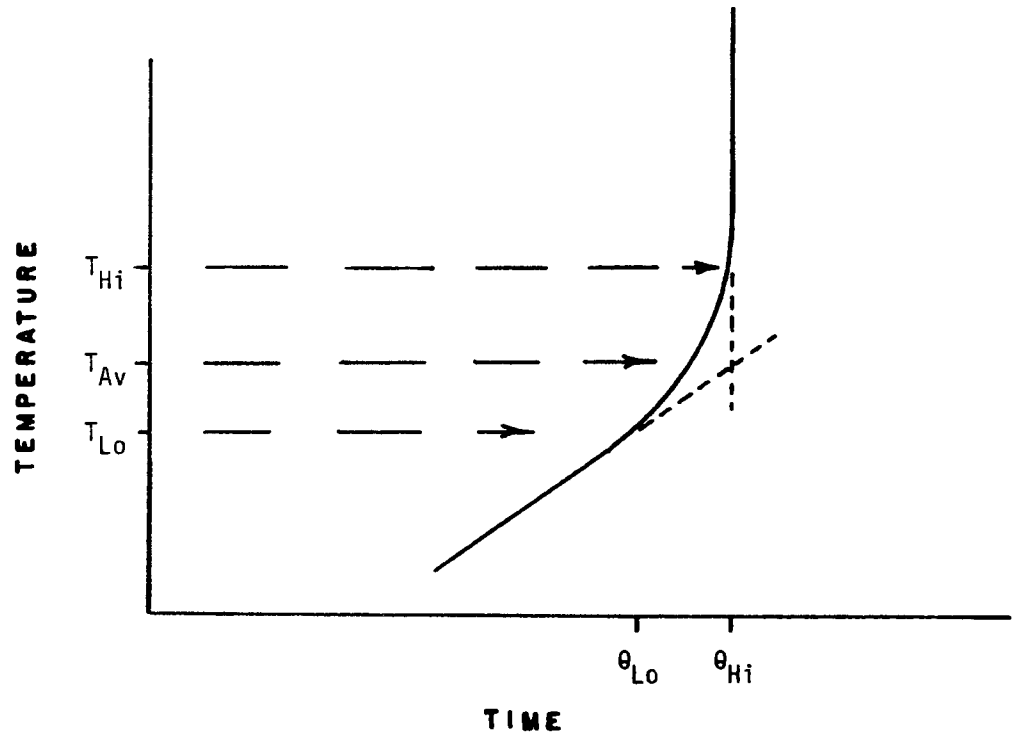
The choice of T_{Av} as the ignition temperature suffers from the disadvantage that the temperature is dependent on the rate of heating.

A measure of the rate of temperature change is given by noting the time lapse ($\theta_{Hi} - \theta_{Lo}$) between the temperature rise from T_{Lo} to T_{Hi} (see Fig. 7). Typically the time lapse was between 30 sec and 2 min depending upon the heating rate prior to θ_{Lo}. Short time differences tended to occur with rapid heating rates, while larger time differences were usually the result of slower heating rates.

8.4 Ignition Data

Tables A-5 and A-6 present data on eighteen ignitions referred to in the Results, Section 4.4. The ignition temperatures recorded in the tables are defined in Section 8.3 in the Appendix.

In the old reactor, the lower bed thermocouple was 0.8 cm above the screen and the upper bed thermocouple was 3.0 cm above the screen. Table A-5 gives a comprehensive summary of the data collected from the old reactor. An equally comprehensive summary of the runs made with the new reactor, Table A-6, was not possible because the time lag between ignitions in various sections of the bed (about 10 sec and less) could not be detected with certainty, especially as not all the recorders presented continuous temperature records.



Massachusetts Institute of Technology School of Chemical Engineering Practice Oak Ridge Station			
TIME-TEMPERATURE TRACE OF IGNITION			
Date 10-14-66	Drawn By GHG	File No. CEPS-X-4	Figure 7

Table A-5. Old Reactor Ignition Temperature Data
(All Temperatures in °C)

Date	Ignition No.	Thermocouple Registering Ignition First					Temperatures at Time of First Ignition				Ignition Temperatures (T_{Lo}) at Different Points in the Bed		
		Position	T_{Hi}	T_{Av}	T_{Lo}	Hottest Point Ignited First	Inlet Air	Screen	Lower Bed	Upper Bed	Screen	Lower Bed	Upper Bed
9-28-66	1	Upper Bed	370	306	265	no	267	273	275	265	no ignition	300	265
9-28-66	2	Lower Bed	430	318	310	yes	-	-	310	308	no ignition	310	300
10-4-66	3	Upper Bed	405	385	370	yes	265	280	320	370	no ignition	316	370
10-4-66	4	Upper Bed	405	362	352	yes	295	318	345	352	318	352	352
10-4-66	5	Lower Bed	357	344	325	yes	277	293	325	307	302	325	no ignition
10-4-66	6	Lower Bed	390	387	305	yes	272	286	305	288	310	305	no ignition
10-4-66	7	Lower Bed	370	347	330	yes	298	313	330	314	341	330	no ignition
10-4-66	8	Lower Bed	360	335	310	yes	282	297	310	292	325	310	no ignition
10-4-66	9	Lower Bed	353	338	337	yes	291	315	337	323	316	337	323

Table A-6. New Reactor Ignition Temperatures, °C
(T_{Lo} Values)

Thermocouple No.	Frit	9	10	11
Distance above frit (cm)	0	0.76	1.52	2.28
Run 1	no ignition	310	317	330
Run 2	no ignition	340	342	342
Run 3	301	320	322	no ignition
Run 4	302	328	322	no ignition
Run 5	300	343	352	352
Run 6	314	347	353	353
Run 7	302	345	342	no ignition
Run 8	310	337	338	no ignition
Run 9	294	318	328	332

8.5 Charcoal Data

The charcoal used in this investigation was a commercial grade charcoal, MSA 27527, Lot #18. Analysis indicated an ash content of 2.02%, a surface area of 1425 m^2/gm, a bulk density of 0.80 gm/cc, and a porosity (internal) of 14.23%. The mesh size was 8-16.

8.6 Sample Calculation of Rate of Heat Generation in the Charcoal Bed Before Ignition

volumetric flow = 3100 cc/min at 25°C at 1 atm.

PV = nRT so that

$$\text{molar flow rate} = n = \frac{PV}{RT} = \frac{3100}{(82)(298)} \text{ moles/min}$$

Using a heat capacity for air (8) of 7.2 cal/gm mole-°K

heating rate = q = molar flow times the heat capacity times the difference between the inlet and outlet air temperatures.

For example, for the 275°C isotherm (see Table 7),

$T_{inlet} = (275 \pm 4)°C$; $T_{outlet} = (298 \pm 4)°C$.

Then,

$$q = (7.2)\left[\frac{3100}{(82)(298)}\right](298 - 275) \text{ cal/min}$$

$$= (0.913)(23 \pm 8)$$

$$= 21 \pm 7 \text{ cal/min} .$$

8.7 Estimation of Heat Losses from the Charcoal Bed

Heat may be lost from the charcoal bed by heat transfer from the bed to the annulus. The rate of heat losses, Q, is given by (2) as,

$$Q = U_o(\pi D_o Z)(\Delta T)$$

where,

$$\frac{1}{D_o U_o} = \frac{1}{D_o h_o} + \frac{\ln(D_1/D_o)}{2k_{quartz}} + \frac{1}{D_1 h_1}$$

D_o = inside diameter of tube = 2.54 cm

D_1 = outside diameter of tube = 2.88 cm

Z = bed height = 3.2 cm

$\Delta T = T_{10} - T_4 = 345 - 319 \doteq 26°C$

These temperatures are for the run in which the sensible heat gain of the air was 50 cal/min (see Profile 5 in Table 7 and Sample OP-10-6-1 in Table A-4).

$$k_{quartz} = \frac{0.016 + 0.030}{2} = 0.023 \text{ cal/sec-cm-°C (7)}.$$

Combining these equations,

$$Q = \frac{\pi Z \Delta T}{\frac{1}{D_o h_o} + \frac{\ln D_1/D_o}{2k_{quartz}} + \frac{1}{D_1 h_1}}$$

Therefore,

$$Q = \frac{262}{\frac{1}{2.54\ h_o} + 2.71 + \frac{1}{2.88\ h_1}}$$

Calculation of the heat transfer coefficient, h_1, is accomplished by using a correlation for heat transfer in an annulus (9).

$$Re = \frac{D_e G}{\mu}$$

where,

D_e = effective diameter of annulus = 5.4 cm - 2.88 cm = 2.52 cm

G = mass flow rate = W/S = 0.0041 gm/sec-cm^2

μ = viscosity of air at 319°C = 0.00029 gm/cm-sec

Therefore, Re = 35.6 in the annulus.

From Jakob and Rees (9),

$$\frac{hr_1}{k} = 3$$

where,

$r_1 = 1/2\ D_1 = 1.44$ cm

k = thermal conductivity of air at 319°C = 1.10×10^{-4} cal/sec-cm-°K

h_1 = 0.000229 cal/cm^2-sec-°K = 1.69 Btu/ft^2-hr-°F

Calculation of h_o is accomplished by using a correlation for packed beds (2) and assuming that the heat transfer coefficient for transfer between the air and the packing is the same as for transfer between the air and the tube wall.

$j_H = 0.91\ Re^{-0.51}\ \psi$ for $Re < 50$

ψ = shape factor = 0.9

$Re = G_o/a\ \mu\ \psi$

G_o = superficial mass velocity = 0.0131 gm/sec-cm^2

From Ref. (2),

$a = a_v(1 - \varepsilon)$

a_v = specific surface = $6/D_p$ = 40 cm^2/cm^3

ε = void fraction = 0.5

Therefore,

a = 20 cm^2/cm^3

Re = 2.4

$j_H = 0.53 = \frac{h}{C_p G_o}(Pr)^{2/3}$

Pr = 0.68 at 345°C

C_p = 7.2 cal/gm mole-°K = 0.248 cal/gm-°K

Therefore,

h_o = 0.0022 cal/sec-cm^2-°K = 16.2 Btu/ft^2-hr-°F

Finally,

$$Q = \frac{262}{177 + 3 + 1520}$$

and Q = 0.154 cal/sec = 9.25 cal/min .

8.8 Sample Calculation of Rate of Heat Evolution from Carbon Dioxide Data

The exit gas sample of Run OP-10-6-1 (see Table A-4), in which the air inlet temperature was 295°C, was found to have the following analysis: 17.3% O_2, 80.8% N_2, and 2.2% CO_2.

2.2/3.7 = 59.5% of depleted oxygen appears as carbon dioxide.

Within experimental error, carbon dioxide could be as high as 2.4% and oxygen could be as high as 19%. In other words, all of the oxygen depleted could have appeared as carbon dioxide.

$$\text{flow rate at exit} = (3100 \text{ cc/min})\left(\frac{78.0}{80.8}\right) = 2990 \text{ cc/min}$$

yields 65.9 cc/min of carbon dioxide which is 0.00294 moles/min of carbon dioxide.

(97,000 cal/mol)(0.00294) = 285 cal/min heat evolved in forming this amount of carbon dioxide.

8.9 Calculation of $T_{charcoal} - T_{air}$

Using the method outlined by Satterfield and Sherwood (18), the temperature difference between the charcoal particles and the air flowing between them can be calculated.

$$q = h\ a\ \Delta T$$

$$q = 50 \text{ cal/min} \cong 0.053 \text{ cal/sec-cm}^3 \text{ where volume} = 15.7 \text{ cm}^3$$

$$h = 0.0022 \text{ cal/sec-cm}^2\text{-°K}$$

$$a = 20 \text{ cm}^2/\text{cm}^3$$

$$\Delta T = \frac{0.053}{(0.0022)(20)}$$

$$= 1.2°C$$

The difference is about 1°C. This difference would be lower at lower temperatures where the rate of reaction would be lower.

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