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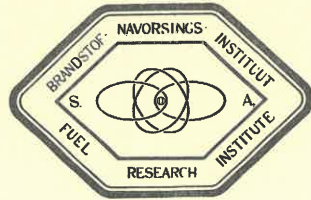
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SUBJECT:
ONDERWERP: THE NORMAL AND HALOGEN INHIBITED COMBUSTION AT

850° C OF COKES OF VARYING ASH CONTENTS.

DIVISION:
AFDELING: CHEMISTRY.

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THE NORMAL AND HALOGEN INHIBITED COMBUSTION AT 850°C
OF COKES OF VARYING ASH CONTENTS.

The combustion of carbonaceous fuels is now recognised as occurring by means of both a heterogeneous (surface) reaction and a homogeneous (gas phase) reaction. While the gas-phase reaction consists in the secondary burning of carbon monoxide to carbon dioxide, there still remains an element of doubt as to whether or not under normal conditions a certain small amount of carbon dioxide is produced together with the carbon monoxide in the primary surface reaction between oxygen and carbon.

Thus the use of halogen inhibitors (chlorine, carbon tetrachloride, phosphorus oxychloride) in the inlet gas stream has served to suppress the gas-phase reaction, but small quantities of carbon dioxide have invariably persisted in the carbon monoxide produced (1), (2), (3), (4), (5).

Loon and Smeets (6) point out that it is not inconceivable that the introduction of such extraneous constituents to the inlet gas may also affect the surface reaction. Grodzovsky and Chukhanov (7) and Tsukhanova (8) (9) many years ago largely suppressed the gas-phase reaction by considerably increasing air-velocity. Using a somewhat similar technique Loon and Smeets (6) extrapolate their experimental curve and conclude that again the possibility of traces of carbon dioxide being produced by a surface reaction is not entirely precluded.

The importance of the inorganic constituents in the behaviour of carbonaceous fuels during combustion and gasification has long been recognised. Earlier extensive work in this field has been summarised by Arthur and Wadsworth (10). More recent work which may be mentioned includes the/.....

the demonstration by Letort and Martin (11, 12) of the significant role of surface oxides and the catalytic effect of a variety of metals on the combustion of graphite at about 500°C. Copper in particular was found to have a superactivating effect. Certain metals were found to have the following order of effectiveness in catalysing the carbon-oxygen surface reaction and increasing the ratio of CO₂ to CO in the product gases:-

Fe, Co, Mn, Ni, Pb, Cu, Ag, Ce, Na, Au (13).

Arthur, also, (13) has found that materials like sodium carbonate and cuprous chloride, apart from rendering the carbon surface more reactive, also increase the ratio of CO₂ to CO in the final product of normal combustion.

In view of this it seemed that it might be profitable to combust a series of cokes of varying ash contents and pure carbon under standard conditions, both with and without the entrainment of a halogen inhibitor of the gas-phase reaction, and to compare the proportions of the two oxides of carbon produced in each case.

For this purpose a series of five cokes, Nos. 28, 31, 32, 33 and 34, all produced in the Institute's experimental coke oven, by blending float and sink fractions of Landau coal and one coke, No.20, likewise derived from Durban Navigation coal, were used. Analysis showed them to have ash contents as follows:

<u>Coke No.:</u>	28	34	33	32	31	20
<u>Ash %:</u>	8.75	9.7	10.2	10.9	11.45	17.85

In addition a sample of spectrographically pure graphite was obtained in the form of waste ends of spectrograph rods from the National Physical Research Laboratory, C.S.I.R., Pretoria.

Cokes Nos. 28, 31 and 34 were subjected to complete ash analysis by Mr. D.W. Gilman with the following results, given as percentages of the whole dry coke:--

	<u>28.</u>	<u>34.</u>	<u>31.</u>
SiO ₂	3.19	3.80	5.11
CaO	0.40	0.46	0.55
MgO	0.20	0.23	0.41
Alkalis as Na ₂ O	0.015	0.010	0.005
SO ₃	0.30	0.35	0.44
Fe ₂ O ₃	0.61	0.57	0.46
TiO ₂ + Al ₂ O ₃	3.40	4.10	5.18
P ₂ O ₅	0.06	0.07	0.09
Total ash (775°C)	8.11	9.51	11.82

The materials were carefully crushed and the -10 + 28 mesh portion retained in each case for use in the experiments.

The furnace used was in all respects similar to that used and described by Bridger and Appleton (5), the lower half of the combustion tube being here also filled with silica chips. Air was supplied from a compressed-air cylinder and measured by means of a graduated capillary flow-meter. When desired a portion of this air could be by-passed through a second capillary flow-meter and then through a bubbler containing carbon tetrachloride before rejoining the main air-stream again.

In the first experiments carried out a thermocouple, dipping into the coke about 6 - 8 cms. below the upper level of the furnace proper, was used to record temperatures - as described by Bridger and Appleton (5). Most anomalous results were obtained, however, and it soon became clear that temperatures about 150°C higher prevailed lower down in the furnace than were present at the thermocouple level. This situation was further aggravated by the fact that the narrow combustion zone, travelling slowly up through the column of coke, could have a temperature some hundreds of degrees higher than its

surroundings/.....

surroundings depending largely upon the amount of air being supplied. The temperature recorded by the thermocouple under these conditions obviously bore no relationship to conditions existing in the immediate surroundings of the actual reaction zone. A considerable but variable amount of carbon dioxide reduction, by reaction with the hot coke, could clearly occur under such conditions.

For these reasons a thermocouple sufficiently long to reach right through the coke column was used, and the wires were withdrawn more or less continuously during the combustion so as to record the maximum temperature of the remarkably well-defined combustion zone as it moved up through the column of coke. It was found that once the ignition temperature of the coke had been reached the air could be turned on and the heating current switched off so that a fairly considerable temperature gradient in front of the combustion zone could be achieved in a short time, thereby further obviating the possibility of any secondary reduction of CO_2 . The temperature of the combustion zone could be controlled by slight alterations in the heating current being supplied to the furnace, if necessary, or by altering slightly the rate of air-supply within the range 85 - 115 litres per hour.

In order to achieve the conditions desired, the following standard procedure was adopted. The sample of coke to be examined (-10 + 28 mesh) was introduced above the silica chips with the thermocouple in position and reaching down to the silica chips. The furnace was then switched on and the coke heated out with a slight passage of air until about 1000°C was reached. After being allowed to cool down to about the ignition temperature of the coke (usually 550°C) the air-flow was adjusted to 100 litres per hour. Suitable exploration with the tip of the thermocouple wires then indicated the position of the slowly moving combustion zone and adjustment of the heating current and/or the rate of air flow (between 85 and 115 litres per hour) adjusted the point of maximum temperature of this zone to the desired $850 \pm 10^\circ\text{C}$. As soon as standard

conditions had been reached, consecutive gas samples, at intervals of about 10 - 15 mins., were taken from the outlet train of the combustion tube and analysed for CO_2 , O_2 , and CO in an Orsat apparatus. In this way about $\frac{1}{3}$ to $\frac{1}{2}$ the coke present in the combustion tube was consumed in obtaining values for uninhibited combustion. Exploration with the tip of the thermocouple wires showed that the hottest position ($850 \pm 10^\circ\text{C}$) of the combustion zone covered not more than about $\frac{1}{2}$ " with a $\frac{1}{4}$ " zone on each side about 10° cooler. Above this combustion zone the temperature fell about 100°C over the first inch and about another 150°C over the next 2 inches - the temperature of the furnace as a whole being in the region of 500°C or less. In one case (coke No. 33) once combustion had been initiated the electric current was switched off and it was found that the desired temperature of combustion could be maintained by the air-draught alone, so that, when the final sample was taken, the furnace temperature had fallen to almost 300°C . In other cases, in order to maintain the required temperature of the combustion zone, it was usually necessary to use intermittent passage of a reduced electric current, the air-flow being maintained at 100 ± 15 litres per hour.

As soon as results for normal combustion had been obtained in this way the temperature of the furnace was raised till the coke was registering a temperature of about 650°C whereupon an air-current of 100 ± 15 litres per hour containing approximately 1% by volume of carbon tetrachloride was passed through the tube. The carbon tetrachloride was introduced by by-passing 10% of the air used through a bubbler containing carbon tetrachloride the temperature of which remained between 10°C and 15°C during the process. Again the temperature of $850 \pm 10^\circ\text{C}$ was maintained by electric heating of the furnace when necessary and by slight adjustments of the air-flow rate within the range 100 ± 15 litres per hour. In the inhibited combustions the zone of highest temperature was apparently
no less/.....

no less sharp but an overall furnace temperature about 100°C higher was required to maintain it at $850 \pm 10^{\circ}\text{C}$ than was the case with normal combustions, and the zones of lower temperature on either side were noticeably wider, particularly ahead of the zone of highest temperature. It seemed clear that interaction of the inhibitor, or its pyrolysis product, chlorine, with the inorganic constituents of the coke, played some part in producing the temperature of the "combustion zone." It was found that if the air-flow were discontinued for a short time and the "combustion zone" temperature allowed to fall somewhat, clogging occurred due to solidification of material in this zone. The distillation of ferric chloride and hexane hexachloride into the cooler parts of the combustion tube and into the gas-outlet train has been noted by previous workers. In these experiments it was noticed that a powerful lachrymatory substance was also produced in this way as well as a substance of apparently orange-yellow colour which readily sublimed into the outlet train and reacted violently with water after the manner of, say, phosphorus pentochloride.

The fact that changes were being brought about in the inorganic constituents of the cokes makes it very doubtful whether any conclusions could safely be drawn regarding the influence of these constituents on the proportions of carbon dioxide and carbon monoxide produced during inhibited combustions.

Combustions Using Pure Graphite:

It had been hoped that a comparison might be obtained between combustions using pure graphite and cokes of varying ash contents. It was found, however, that the pure graphite used did not ignite with air under the same conditions of furnace temperature (550°C) as did the coke samples, a temperature of approximately 100°C higher being necessary, and moreover, that once combustion had been initiated it was necessary to maintain the temperature of the furnace as a whole at about this temperature in order that combustion might continue. Furthermore/.....

Furthermore the smooth nature of the graphite particles coupled with the absence of (supporting) ash apparently caused a constant descent of graphite particles in order to replace those which were being combusted. The combustion zone therefore remained more or less constant in position (as indicated by exploration with the thermocouple tip) and, due to the somewhat intermittent descent of particles, smooth standard combustion conditions were virtually impossible to attain. Moreover, the amount of "void" between the particles was highly variable under such conditions, which would explain the considerable variation in the gas analysis results obtained.

Again in the case of inhibited combustion it was found that a temperature between 750°C and 800°C had to be maintained for the furnace (compared with about 650°C or less for the cokes used) in order to achieve combustion at 850°C as before. Moreover it was found when the combustion tube was finally emptied that a considerable portion of the graphite had been converted to fine powder so that the results obtained referred to material of a particle size etc., very different from that of the cokes used.

The results obtained for pure graphite were as follows:-

<u>Uninhibited:-</u>	<u>Average:</u>
CO % = 16.0 15.4 17.8 14.6 16.6 14.4 15.0	15.7 %
CO % = 7.2 8.2 3.8 9.8 5.8 9.8 9.0	7.7 %

<u>Inhibited:-</u>	<u>Average:</u>
CO ₂ % = 3.8 3.8 4.2 3.8	3.9 %
O ₂ % = 5.6 5.4 3.6 2.8	4.35 %
CO % = 21.6 21.2 23.6 25.2	22.9 %

Combustions Using Cokes Nos. 28, 34, 33, 32 and 31.

<u>No. 28. Uninhibited.</u>	CO ₂ % = 13.6 14.2 14.2	<u>Average:</u> 14.0%
	CO % = 10.8 10.2 10.2	10.4%
<u>Inhibited:</u>	CO ₂ % = 5.6 5.2 5.2	5.3%
	O ₂ % = 0 0 0	0 %
	CO % = 24.4 26.6 26.6	25.9 %

/.....

						<u>Average:</u>	
<u>No. 34.</u>	<u>Uninhibited:</u>	CO ₂ % =	15.2	15.0	15.2	15.2	15.2 %
	(9.7 % ash)	CO % =	8.8	8.4	8.4	8.8	8.6 %
	<u>Inhibited:</u>	CO ₂ % =	6.4	5.0	6.2	6.6	6.1 %
		O ₂ % =	0	3.2	2.2	2.8	2.1 %
		CO % =	24.4	22.0	22.6	20.4	22.4 %

						<u>Average:</u>			
<u>No. 33.</u>	<u>Uninhibited:</u>	CO ₂ % =	15.2	15.0	14.0	14.8	14.4	14.6	14.7 %
	(10.2 % ash)	CO % =	8.4	9.4	10.6	10.0	10.0	10.0	9.7 %
	<u>Inhibited:</u>	CO ₂ % =	4.8	4.6	5.4				4.9
		O ₂ % =	1.0	2.4	1.0				1.5
		CO % =	26.0	24.6	24.6				25.1

						<u>Average:</u>			
<u>No. 32.</u>	<u>Uninhibited:</u>	CO ₂ % =	16.2	15.6	16.0	15.6	15.2		15.7 %
	(10.9 % ash)	CO % =	7.2	7.6	7.2	7.6	8.2		7.6 %
	<u>Inhibited:</u>	CO ₂ % =	4.0	4.8	7.0	5.8	6.0	5.6	5.5 %
		O ₂ % =	1.6	0.2	0.8	0.2	0.4	1.0	0.7 %
		CO % =	26.4	26.6	22.6	25.6	25.6	24.8	25.3 %

						<u>Average:</u>			
<u>No. 31.</u>	<u>Uninhibited:</u>	CO ₂ % =	16.2	17.0	17.8	17.8	17.2		17.2 %
	(11.45 % ash)	CO % =	6.6	5.0	4.0	4.0	4.8		4.9 %
	<u>Inhibited:</u>	CO ₂ % =	4.8	5.8	5.2	5.6	6.2		5.5 %
		O ₂ % =	0.8	0.6	0.7	0.6	0.4		0.6 %
		CO % =	26.2	25.0	25.8	25.6	24.8		25.5 %

Taking/.....

Taking the average figures in each case we have:-

Coke No.	% Ash.	<u>Uninhibited.</u>		<u>Inhibited.</u>		
		% CO ₂	% CO.	% CO ₂	% O ₂	% CO.
28	8.75	14.0	10.4	5.3	0.0	25.9
34	9.7	15.2	8.6	6.1	2.1	22.4
33	10.2	14.7	9.7	4.9	1.5	25.1
32	10.9	15.7	7.6	5.5	0.7	25.3
31	11.45	17.2	4.9	5.5	0.6	25.5

The only clear-cut indication contained in these results is the increase in CO₂ for normal combustions which roughly parallels the increase in ash content except for cokes Nos. 34 and 33 where the results do not quite follow the apparent sequence of the others. No sequence is shown in the inhibited combustions, though this is perhaps of doubtful significance in view of what has already been said regarding the obvious interaction between inhibitor and ash constituents. Here, except for cokes Nos. 34 and 33 the results are of approximately the same order.

It is highly probable that these results are related to the content of one or other, or a combination of certain, of the ash constituents but a very much more detailed investigation would be required to confirm this. In this respect the results may be taken as confirming existing knowledge of the subject (10, 11, 12, 13 etc.).

Combustion of Coke No. 20:

The following results were obtained for coke No. 20 (17.85 % ash):-

					<u>Average:</u>	
<u>Uninhibited:</u>	CO ₂ % =	14.6	15.6	15.2	13.8	14.8 %
	CO % =	10.2	7.6	7.8	10.6	9.1 %
<u>Inhibited:</u>	CO ₂ % =	4.8	5.4	5.4		5.2 %
	O ₂ % =	1.0	1.2	0.4		0.9 %
	CO % =	25.0	24.6	25.4		25.0 %

It will/.....

It will be seen that these results are in all respects very similar to the figures obtained for coke No.33 where the ash content was only 10.2%. It is thus clear that if, as is believed to be the case, the overall results obtained are ascribable to certain of the inorganic constituents present in the cokes examined, coke No. 20 must have a combination of such ash constituents which give the same final activity as those of coke No.33.

It had originally been hoped, as will be clear from the introduction, that the results obtained from the inhibited combustions might give information as to the extent of the formation (if any) of carbon dioxide by a surface reaction correlated with ash content or constitution. For reasons already given it is now clear that such cannot be expected.

The results as a whole do, however, emphasise the importance of the inorganic constituents of carbonaceous fuels in determining ignition temperatures, proportions of carbon monoxide and dioxide produced during normal combustion, and hence bad temperatures and other effects.

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PRETORIA.

3rd July, 1950.

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