COMBUSTION PROCESSES IN PULVERISED COAL:

THE BURNING TIMES OF SINGLE COAL PARTICLES.

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for the Degree of

Doctor of Philosophy

by

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PREFACE

The work described in this Thesis forms part of a general programme on problems in Pulverised Fuel Firing commissioned by the Electricity Supply Research Council, and being investigated under the direction of Professor M.W. Thring in the Department of Fuel Technology and Chemical Engineering, University of Sheffield.

I have great pleasure in recording my thanks:

to the Research Council for their most generous financial support, and their unfailing and encouraging interest in the progress of the work;

and to Professor Thring for his initial presentation of the problem, and for his active interest and helpful advice in the subsequent development of the work.

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SUMMARY

Burning times of captive coal particles have been measured as a function of particle size for 10 different coals ranging in rank from 5% V.M. to 40% V.M. Similar measurements have been made before, but in this investigation captive coal particles have been used for the first time, and, partly as a consequence of the captive technique developed, it was found possible to split the total burning time into its two components of volatile and residue burning times.

In these experiments, the particles ranged in size from 300 microns to 4 mm., and in weight from 20 micrograms to 80 milligrams. They were made captive by cementing them to fine silica fibres, and they were then burned between a pair of electrically heated wire coils. These coils were made of resistance wire wound in flat spirals and set up with their planes horizontal 1.5 cm. apart. The burning times were measured by picking up the radiation from the burning particle with a photocell and recording the signal obtained with a fast pen recorder. Separation of the burning time of the volatiles from that of the residue was possible because the trace obtained from the

flickering volatile flame was so characteristically different from that generated by the steadier residue combustion. The measured times were found to be insensitive to coal rank; and, for the particle size limits given, ranged from 0.5 sec. to 15 sec. for the volatile combustion, and from 1 sec. to 200 sec. for the residue combustion.

Theoretically, the results for the residue combustion were found to be in good quantitative agreement with the square law relationship between burning time (t_b) and initial particle diameter (d_o) derived from the diffusion hypothesis of reaction control:

$$t_b = K.d_o^2$$

The measured values of the power of the diameter were close to 2; and the experimental values of the burning constant (K) for the ten coals ranged from 1000 to 2000, as compared with their theoretical values, predicted from the diffusion equations, which ranged from 1500 to 2500. The average ratio of the predicted and experimental values of K was 1.5, and consideration of neglected factors such as swelling showed that, if these factors are taken into account, the predicted values of K should be reduced, thus improving still further the agreement between prediction and experiment. In contrast, the relation between burning time and diameter predicted from the chemical hypothesis of reaction control was a linear one, with unity for the predicted value of K. This clearly ruled out the possibility of chemical reaction control over the size range examined.

On the other hand however, prediction of burning times in flames indicated that, in the P.F. size range (1 to 100 microns), with limited excess air, the chemical and diffusional factors may well be comparable, so that, in extrapolating to this size range, care should be taken to ensure that all possibly relevant factors have been taken into account.

1. INTRODUCTION

Knowledge of burning times of coal particles is required in connection with pulverised fuel firing, this being a type of firing in which finely ground coal dust is carried into a combustion chamber on a stream of air. The coal particles are of sizes lying mostly in the range 1 to 100 microns, and, as they enter the combustion chamber, they are ignited by heat transferred back from the flame (either directly or indirectly) and they burn out - or are expected to do so - as they traverse the chamber.

Whether or not the particles do in fact burn out completely before leaving the combustion chamber obviously depends upon their burning times being less than their residence times, these latter being controlled mainly by the macroscopic aerodynamics of the combustion chamber. Since burning times must therefore be correctly matched to residence times this provided a convenient basis on which to split the overall flame problem into two components for research purposes. Some experiments, concurrent with those being described here, on the measurement of residence times have already been reported (1,2); this present thesis is concerned with the complementary measurements on burning times of single coal particles, and the possible relevance of these to flames, thus supplementing and amplifying what has already been reported elsewhere (3,4).

Estimation of burning times can be made either from calculation or from experiment but, since burning times are known to be a function of parameters and ambient conditions such as particle size, particle temperature, gas temperature, relative velocity and oxygen concentration, calculations must be backed by suitable experiments designed either to check the validity of any function of the relevant parameters that was predicted from theory, or to determine a suitable function empirically. Estimation from experiment is of course possible, either by direct measurement on the full scale industrial plant when built, or by empirical extrapolation without the use of any theoretical functions, from data obtained from other systems; but the first of these alternatives is clearly of no use to the designer of that plant since it puts the cart before the horse. The second alternative of empirical extrapolation is very largely guesswork that, if applied to conditions too far remote from the range of the initial measurements could easily be inaccurate by an order of magnitude. Extrapolation can only be trusted if the method of extrapolating is to use a function containing all the significantly relevant parameters;

this again is a problem of calculation which therefore beings us back to the starting point, the validity of such calculations. If the basis of any proposed function is empirical we can set up the same objection that was raised to the use of empirical extrapolation, namely that they are only to be trusted inside the experimental range over which they have been shown to hold. In contrast, a function derived from first principles can be used with much greater confidence as a basis for extrapolation, provided only that there is good reason to believe that all the significantly relevant parameters have been included in the theory.

Theories to predict burning times, containing all the significantly relevant parameters (or so it was believed at the times they were formulated), have been constructed (5 - 12); data on which the theories may be tested are however less plentiful than might be desired. Data have been obtained both from flames (13 - 18) and from single particles (19 - 27); but data from flames are particularly liable to error in our present state of knowledge since flames are generally too complex, either for accurate control and independent variation of variables, or for unambiguous interpretation of the results obtained. For example, in a flame with recirculation, the histories of particles sampled at the same point will vary since some will have travelled straight from the burner to the sample point, but others may well have recirculated one or more times before being collected by the solid sampler. Interpretation of such results is therefore ambiguous. To avoid this ambiguity in investigations of the combustion mechanism, the usual practice is to use single particles whose histories can then be followed and documented as fully as possible.

Even with single particles however there is often some indetermination; this for instance is nearly always true of free particles projected through a furnace, since the relative velocity is unknown, variable, and uncontrollable. Such indetermination had been met previously (21 - 24) in connection with problems of carbon combustion, and had been solved for those problems by the use of captive particles that could then be subjected to a previously determined and controllable history. Though this captive particle technique is not known to have been previously applied to coal, it seemed nevertheless the one most likely to produce results, if it could be so applied: and so it has proved. The development of such a captive particle technique that could be applied to coals therefore became the primary technical objective of the work being reported here; also reported are the results obtained with the technique developed using particles of different sizes obtained from 10 different coals covering the range in rank from 5% V.M. to 40% V.M. Also discussed is the possible validity of the results, when extrapolated, to predict the behaviour of particles in a flame.

2. HISTORICAL

That so little is still known for certain about the behaviour of burning particles in a flame may seem somewhat surprising in view of the fact that commercial exploitation of P.F. firing has a history going back at least 75 years and maybe more, and that proposals, patents and experiments on the system go back a further 75 years. The reason for this would seem to be that for many years the problems chiefly encountered were of a technical or technological character arising in connection with such problems as the quality and reliability of refractories, fans, grinding plant, feeders, and the auxilliary units generally. For example, Crampton (28) in 1869, describing some of his extensive experiments, reported that "I have ascertained that rapid wear and waste of the refractory material composing this chamber or furnace are caused by the impinging stream of fuel and air, which are far more destructive than would have been anticipated without practically testing their operation," and he continued that this waste would have to be avoided if the expense of replacing the refractories was not to nullify the advantages of the system. This in fact was a crucial point, that we can appreciate very much more in retrospect since, from the earliest experiments, there seems to have been no real difficulty in establishing the flame; indeed the real difficulty was to prevent slagging of the ash, which occurred in Cramptons combustion chambers, and that we now know is particularly injurious to the refractories. In steam raising boilers particularly this problem was not really overcome until the 1920's with the introduction of the water screen and water wall for the dry bottom furnaces, and the roughly parallel introduction of the wet bottom or slag tap furnace specifically designed to cope with the slagging of the ash. Previous boilers, even the specially designed Bettington boiler of 1905, were always bedevilled by uncontrollable slagging. These refractory difficulties now make it clear to us in retrospect why the two years 1895 and 1919 are highlighted as crucial dates in the history of P.F. firing. By 1895 commercial exploitation of P.F. was well under way, for instance at the Berlin exhibition in that year a number of industrial firms exhibited pulverised fuel equipment that they were marketing commercially (29). Indeed, as early as 1873, Cochrane (30) mentions in the discussion on Cramptons paper (28) that a few months previously he had inspected a pulverised fuel incinerator in daily use in Chicago. It is true that many of the original plants were so prone to operational difficulties that after variable periods of testing their use was discontinued (though it should also be remembered that, after some period of trial, commercially successful plant are unlikely to be remarked upon, and therefore mentioned in the literature as having succeeded). However it is also clear that by 1890 P.F. was an accepted alternative in a number of instances to grate firing; particularly so it would seem for disposing of colliery waste that otherwise could not be utilized (31). Even so it was still only an alternative, and it was not till the late 1920's with the development of boilers evaporating at upwards of 250,000 lb/hr. that an era was introduced in steam raising in which the use of P.F. was unchallenged. The significance of the cement industry's use of P.F. in 1895 would therefore seem to be that here was an application in which P.F. firing, being entirely suitable, was immediately and completely successful, so much so in fact that its use soon dominated the cement industry and has remained virtually unchallenged in it ever since. The development of boiler firing however was less spectacular, even though some of the earliest experiments and applications were on steam raising. In 1905 the first boiler ever to be designed specifically for P.F. firing came into use. This, the Bettington boiler, was being marketed in this country and abroad for the following 20 years or so. These had a considerable steam capacity for their date: in 1913, three of these boilers, each of 20,000 lb/hr., were installed at New Waterford in Nova Scotia. These boilers however never really developed further and the real development of the water tube boiler came with Andersons introduction of the water screen in 1919. By 1925 this had developed logically into the fully cooled water-wall boiler.

Because of this natural preoccupation with the technical (and also economic) aspects of the P.F. system, the combustion engineers gave little or no attention for many years to the more fundamental aspects, particularly with regard to the physical chemistry and aerodynamics of the system. Until the 1920's most of the fundamental research on the combustion mechanism of coal particles was done in connection with coal dust explosions in coal mines, and for the first quarter of this century this provided much of the fundamental data required in P.F. combustion. The best example of this was the use by de Grey (32), in connection with P.F. burner design, of Taffanel and Durr's (33) data on flame speeds obtained during explosion research for the Comité Centrale des Houillères de France. Orning (34) is of the opinion that the data are likely to be qualitatively correct (so that de Grey's burner design principles still stand) but that quantitatively they should be treated with reserve, except as order of magnitude values; even so the curves have been widely reproduced and are still in use today as the only data extant on flame speeds in large coal flames. In comparison with other data (35 - 39) of burning velocity in small flames discussed elsewhere (40), only Taffanel and Durr's values(between 10 and 15 m/sec.) were comparable with speeds found in industrial furnaces; in contrast, the burning velocity values were of the order of 0.1 m/sec. Recent measurements by a colleague (41) using a furnace deliberately designed to cut out recirculation have given flame speeds of about 1 m/sec., in agreement with a thermal theory of flame propagation utilizing only radiation. To increase these speeds by a factor of 10 or 15 requires an additional major mechanism of heat transfer that, it is thought, can only be provided by recirculation. In affecting the reaction rate, the reduced oxygen concentration caused by the recirculated gases is thought to be more than offset by the increased temperature.

Another development from the explosion research was the laboratory test inflammator that, as described by Godbert (42) and Brown (43), assumed many forms. One particular form was the vertical furnace test as used in the British Coal Dust Experiments (44), and subsequently developed into the G - G standard test apparatus (45,46).

In these tests small samples of dust were blown through the furnace to see whether or not they would inflame. Sinnatt and his collaborators (47) used in effect the same system in some carbonization and combustion studies, but using mainly single particles. Subsequent work using this technique already mentioned in passing (19,20,25,26) showed: firstly, the need to specify the particle history more closely; and secondly, the need for more accurate knowledge on a simpler material. Both these requirements were met to some extent by the work on captive carbon particles (21 - 24, 27), but, so far as the work on burning times of coal particles is concerned, this is less plentiful than the literature listed above would suggest. The relevant theories (5 - 12) all led more or less explicitly to the square law equation for burning time,

$$t_b = K.d_o^2 \tag{1}$$

where t_b is the burning time; d_o is the initial diameter; and K is the burning constant. In theory this equation holds for liquid drops as well as for solid particles, and Fig. 1, with Table 1, quoted from a review (48) list most of the known data for both liquid and solid fuels (49,50,11, 12,51,14,25,19). In contrast to the 11 investigations on liquid fuels, there are only 4 listed that were concerned with coal, and of these one set of results was a summary of the first results obtained during this present investigation.

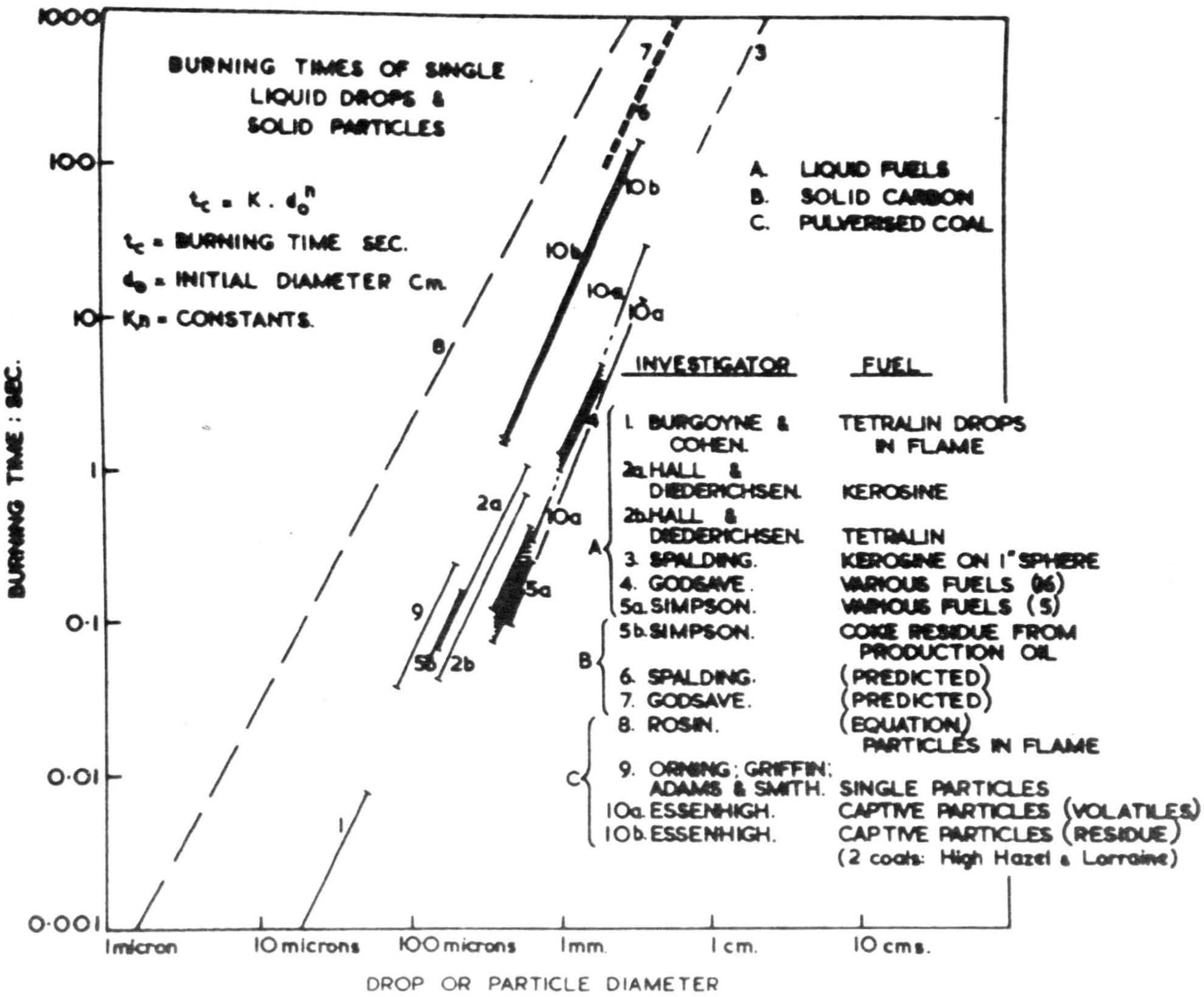


Fig. 1 - Variation of burning time of various liquid and solid fuels with drop or particle diameter

TABLE 1

Values of the Burning Constant K (sec/cm^2)

	Investigator	Fuel	K	Range of drop or particle diameter microns
	(A) LIQUID FUELS			
1	Burgoyne and Cohen (49)	Tetralin drops in flame	312.5	8 to 50
2a	Hall and Diederichsen (50)	Kerosine	300	150 to 600
2b	Hall and Diederichsen (50)	Tetralin	195	150 to 600
3	Spalding (11)	Kerosine on 1 in. spheres	150	(Equation tested indirectly)
4	Godsave (12)	Various fuels (16)	100-130	1000 to 2000
5a	Simpson (51)	Various fuels (5)	60-100	350 to 650
	(B) SOLID CARBON			
5b	Simpson (51)	Coke residue from production oil	330	135 to 220
6	Spalding (11)	(Predicted)	2000	-
7	Godsave (12)	(Predicted)	2060	-

TABLE 1 (Cont'd)

	Investigator	Fuel	K	Range of drop or particle diameter microns
		(C) PULVERISED COAL		
8	Rosin (14)	Equation-particles in flame	4360	-
9	Orning (25); Griffin, Adams and Smith (19)	Single particles; (free in furnace)	625	80 to 200
10a	Essenhigh	Single captive particles-volatiles	$100(L)^x$ $131(H.H)^x$	650 to 4060
10b	Essenhigh	Single captive particles-residue	$988(L)^x$ $1424(H.H.)^x$	325 to 4060

^{x}L: Lorraine; H.H: High Hazel

3. FORMULATION OF PROGRAMME

3.1 Formulation of Requirements - As there was clearly a need, and scope, for a more detailed examination of burning times of coal particles, (particularly with respect to a range of coal rank), this therefore became the scientific objective of the work being reported here, in conjunction with the technically desirable requirement (as explained in the Introduction) that the particles of coal used in the investigations should be captive. With the general objective thus defined, the next problem was the selection of the particular parameters to be investigated. The programme finally adopted was inevitably a compromise between what was theoretically desirable and what was immediately practicable.

What is theoretically desirable is to know, or to discover, the complete laws governing the rate of combustion of a particle in a flame so that its history can be fully predicted. What this involves can be deduced from a qualitative consideration of the particle behaviour as it traverses the flame. As the dry coal particle enters the furnace, carried on the stream of almost cold primary air, it enters a radiation field that increases in intensity as it approaches the flame front; and in consequence it heats up, though simultaneously losing some heat by conduction and convection to the cold ambient air. At the same time there is likely to be some degree of mixing with hot combustion products recirculated back from the flame. These will have the dual effect of reducing the oxygen concentration but of increasing the ambient gas temperature so that the effective heat capacity (or thermal load) of the primary dust stream is reduced. Since it heats up faster, it may ignite sooner. As the particle enters the flame front it will have been sufficiently heated to expel an inflammable volume of combustible volatiles that will then burn in any oxygen available. When volatile emission ceases oxygen attack on the solid residue can start; on this point there is some evidence presented elsewhere (48) based partly on Orning's work (25), that for a given particle the events are consecutive and do not overlap, though there is overlap between different sized particles. As combustion proceeds the oxygen is progressivly depleted though this depletion will be modified by the volume of secondary air and its method of introduction. The temperature may vary and so may the relative velocity.

In attempting to predict the quantitative behaviour of a particle in a flame, we must first deduce the laws governing its behaviour under the following conditions:

The particles of varying size and coal rank must be sited, captive, in a variable and fully controllable convection/radiation field (to simulate the different degree of relative recirculation), and the ambient gas must be variable in temperature, velocity and composition. We must therefore determine the functions governing:

(1) The variation of burning time with particle size for both volatiles and residue, with the rider that the percentage of volatiles evolved during combustion must also be determined.

(2) The variation with time of (i) particle weight
(ii) particle temperature
(iii) particle size.

3.2 <u>Selection of Parameters</u> - The selection finally made was item (1) above, the variation of burning time with particle size, without the rider on the volatile percentage evolved. My original intention was to study particles of a single coal under different ambient conditions, but specifically to study the differential effect of heating by radiation and by convection since this is a new parameter never before specifically examined, though its importance is becoming increasingly evident. The method of experiment initially proposed to implement this idea was to mount the particles in a tube carrying hot air and simultaneously to irradiate them by the lamp and mirror method devised by the Fire Research Board (52) for their experiments on ignition by radiation. However, during discussions on this proposal, Professor Thring suggested that a small Helmholtz coil of resistance wire might be a more convenient radiation source, and later Dr. Price proposed, as a further modification, the use of a pair of coils wound in a flat spiral in place of the single turn of the Helmholtz coil. On trying this latter suggestion it was found to meet the requirements perfectly.

Before trying to mount the coils in the tube to carry out the experiments as originally conceived, the coils were first tested unenclosed as a combustion device on their own, and with the particles held between the coils on the end of silica fibres to which they were cemented. From these preliminary experiments several important points emerged. Firstly, this technique solved a problem envisaged but hardly investigated up to this point; this was the question of the actual technique of burning the particles. In previous experiments on captive carbon particles (21 - 24) it had been the practice to bring the particles up to the reaction temperature, in the furnace, in a stream of nitrogen, but this could not be done with coal since the particles would carbonize. Alternatively, in the free particle experiments (19,20,25,26) the particles were plunged directly into a preheated enclosure, but again preliminary experiments on the effect of shock heating, using a small fast-heating pedestal heater similar to that described by Orning (25), showed that the particles were liable to explode. Fortunately the coil technique described above solved this problem since, with the particles already in position, the coils heated up fairly rapidly but over a sufficient period of time to reduce the thermal shock to the point where only the larger particles occasionally exploded. The second point observed during the preliminary experiments was that the particles burned only if they were in the hot convection current generated by the coils, even though the radiation intensity from the coils (at about 1000° C) was high enough to cook off the volatiles. Later experiments (53) on light and heavy oil substantiated the tentative conclusion that, for the carbon residues to burn out, they required a minimum air temperature as well as a minimum temperature of the solid. Thirdly, on testing the method devised for measuring the burning time, by picking up the radiation emitted by the particle with a photocell and recording it, this was found to be sufficiently sensitive to distinguish between the volatile and residue combustion, and this clearly was a fact that could usefully be taken advantage of. Finally, this experimental set-up was found to be easily adapted to include a device for quenching the particles at the end of the volatile combustion. The object of this was to determine the volatile loss at that point in the reaction since there was reason to believe that not all the volatile content normally determined by volatile analysis was evolved (54). The chief basis for this belief was some research on coal dust explosions carried out early this century which established that in laboratory inflammator tests (55,56) only a fraction of the volatile content was inflamed; and that in explosion flames (57,58) there was evidence that some flames were "inflammations" involving mainly volatiles, but most were "explosive combustion" in which the coal particles burnt as units without any distillation whatever. Evidence from burning times (57) is thought (48) to support this view. This explosion work led to the formulation of the Two-Component hypothesis of coal constitution by Clark and Wheeler (59) that, recently revived and elaborated (54,60), has been summarised elsewhere (61); the significance of this hypothesis is that it explains to some extent why a split in the volatiles may possibly occur. If an explosion flame is too fast to allow devolatilization, this may still not occur completely even in the much slower reacting P.F.

flames since there is evidence (62) that the free hydrogen (the Component IIa,61) was so firmly bound in with the fixed carbon that the time taken for its removal was significantly longer than the burning time in the P.F. flame. To test this hypothesis some quenching and carbonization experiments were carried out and have been fully reported (3). Whilst these experiments were not really conclusive either way and require supplementary tests, the indications provided were: (1) that some volatile material equivalent to 20 or 25% of hydrogen by atomic proportions was retained; but (2) that though this quantity might affect the combustion properties significantly, it was only 1 or 2% by weight and therefore to a first approximation could be ignored, though carrying the rider that the solid residue left from the devolatilization might be more reactive than pure carbon. These experiments were therefore suspended in favour of the more immediately important ones on measurement of burning times.

On returning to the main experiments I then had the choice: either of continuing with the original plan to test a single coal in a tube under controlled convection and radiation; or of continuing with the experiments using the unenclosed coils. In view of the knowledge gained by that time that the technique already developed would split the burning time into its two components, and thus provide measurements not previously made in detail, the programme was thereupon recast to examine the following parameters:

Using the coils sited unenclosed, as described, burning times from the volatiles and residues were measured, at fixed oxygen partial pressure, in the radiation/low intensity convection field generated by the coils, as a function of: (i) particle size

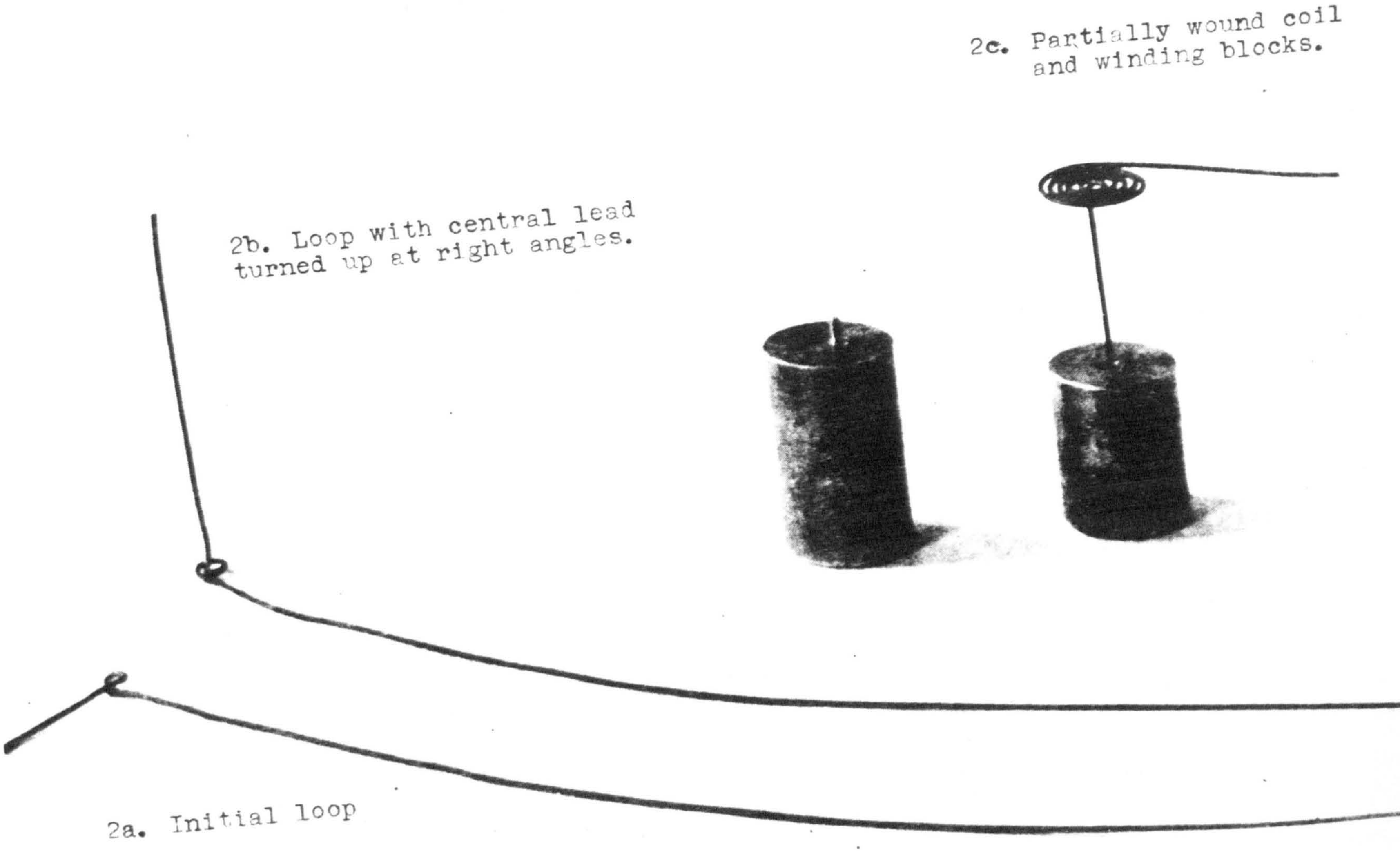
(ii) coal rank.

4. EXPERIMENTAL

4.1 Apparatus - As outlined above, the chief components of the apparatus used were two heating coils of resistance wire to burn the particles, and a photocell to follow the burning.

The heating coils were made from 18-gauge Nichrome V resistance wire wound by hand round a lug in a brass block so that they formed flat spirals. To keep the coils flat during winding they were wound between the faces of two brass blocks, one of which carried the winding lug. Figs. 2(a), (b) and (c) illustrate the stages in construction of a coil, and Fig. 2(d) shows a completed pair of coils mounted in two porcelain connectors strapped to a carrying block.

The finished coils had five complete turns giving them a diameter of 2-cm., and were mounted as illustrated (Fig.2d) with their planes horizontal and 1.5-cm. apart. The power supply to the coils was provided by a fixed mains/low-voltage transformer that could deliver 60 amps maximum, and whose output was controlled by a Variac transformer on its input side. For the majority of the experiments the coil heating current used was 25 amps, which gave a coil temperature, indicated by a fine thermocouple hooked onto the inside of the coil, of about



2c. Partially wound coil and winding blocks.

2b. Loop with central lead turned up at right angles.

2a. Initial loop

Fig. 2 - Method of coil construction

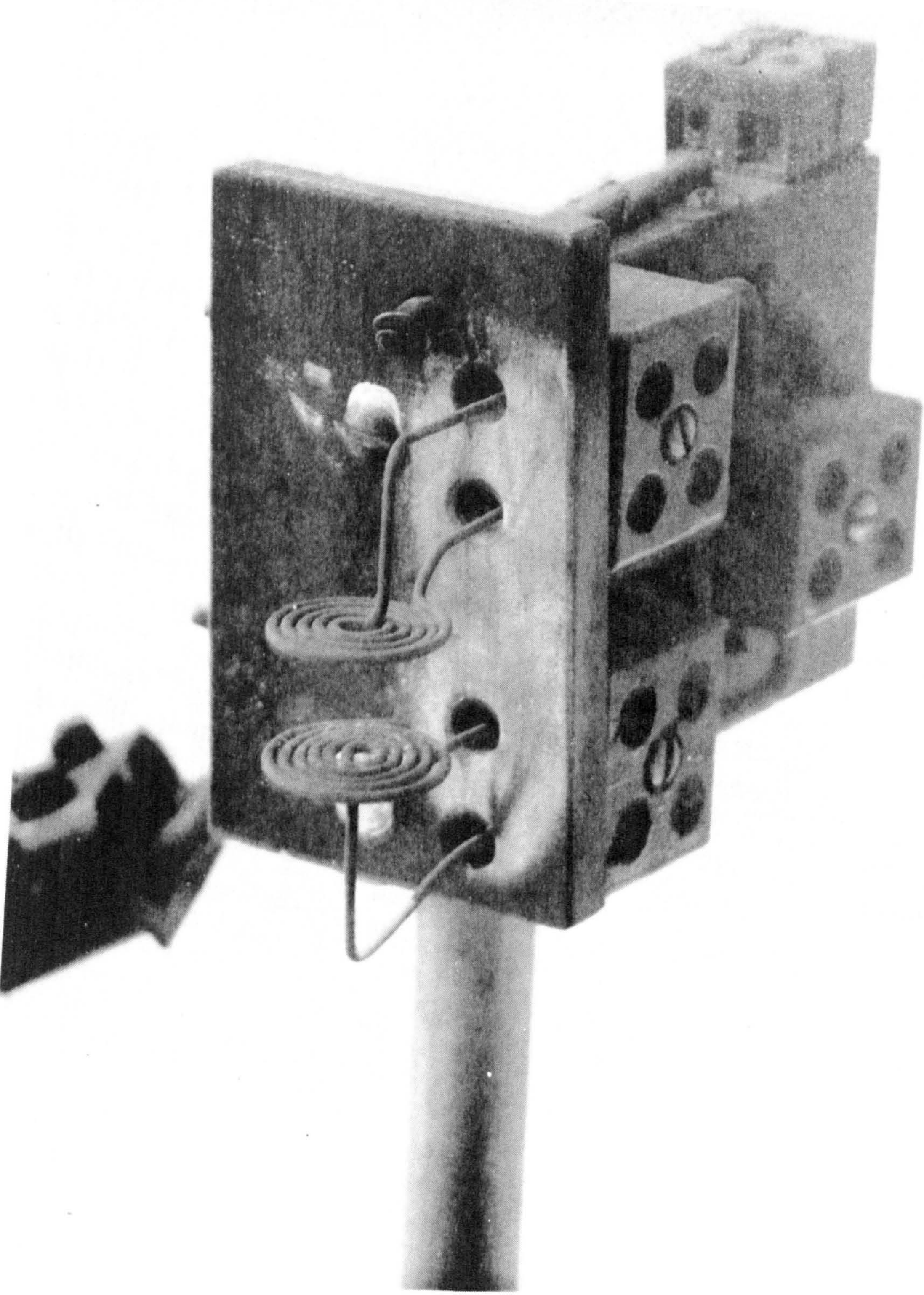


Fig. 2d. - Method of mounting finished coils

1000° C. The coal particles were held captive between the coils by cementing them to silica fibres with a high temperature cement.

Radiation from the burning particles was picked up by a photocell focussed onto it by a lens, - the photocell, lens and heating coils all being mounted on an optical bench. The lens and photocell were so placed that the image of the coils was focussed just outside the photocell aperture so that the signal from these was kept to a minimum. Considerable background reflection from the coils, via the bench and the walls, made light shielding necessary round the lens and photocell to reduce this background. The general arrangement is shown diagrammatically in Fig.3. The signal from the photocell was fed to a recorder via a D.C. pre-amplifier. Initially a Cossor C.R.O. was used for recording, the trace being photographed, but this was replaced at an early stage by a Southern Instruments fast pen recorder capable of responding to 66 c.p.s. This sensitivity of response required full electrostatic screening on all leads and components to cut out mains frequency pick-up. At the full gain used, the base line was then barely affected by the background radiation, provided the units were properly focussed, and since the records were used

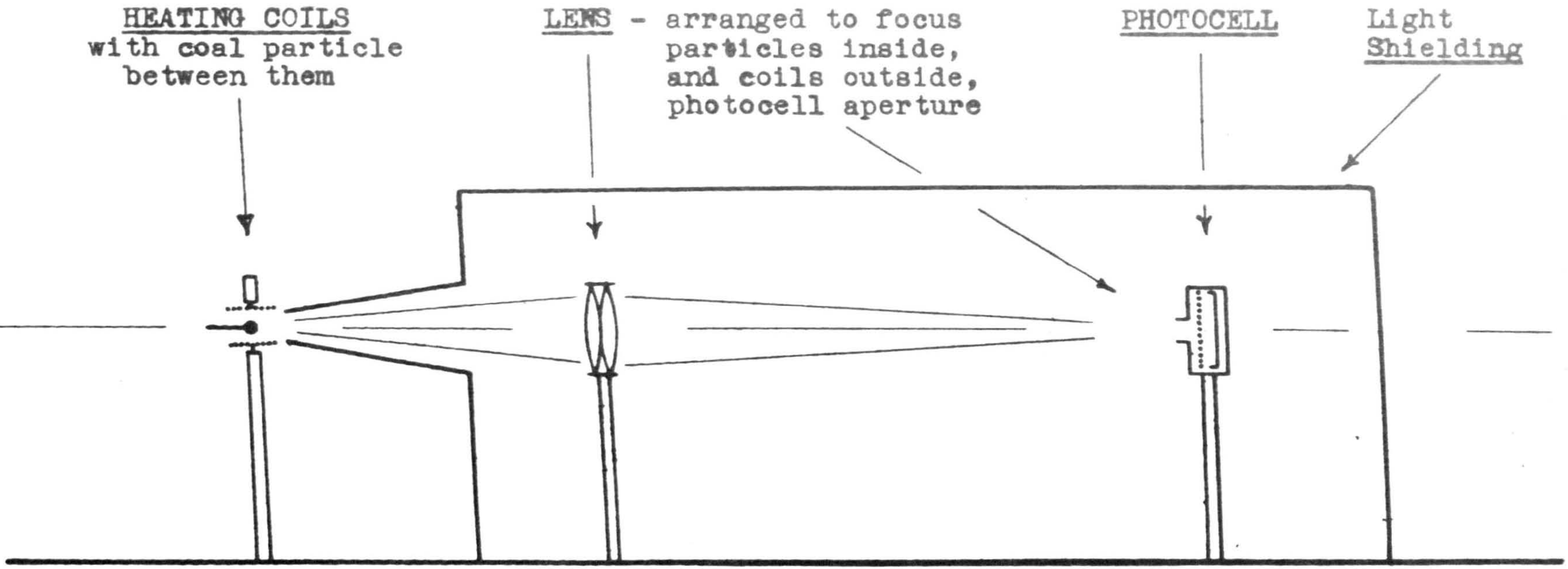


Fig. 3 - Diagrammatic arrangement of heating coils, lens and photocell; also showing the relative position of the light shielding.

only for measuring times and not amplitudes this baseline shift was quite acceptable.

4.2 Coal Preparation - Ten coals were used in these experiments. Their analyses are given in Table 2; the superficial density quoted was measured by a water displacement method. All ten coals were crushed, and then sized by sieving into 16 fractions. The sieving was done by machine using the complete range of B.S. sieves from 3/16" down to 52 mesh (295 microns), and the particle diameter was taken as the arithmetical mean of the two meshes defining each fraction. The range of meshes, with their sizes and means, is given in Table 3.

Although the particles in each sieve fraction were nominally the same size this obviously was far from being true in practice since, in any given sieve fraction, there was some range in size and considerable range in shape. As some selection had to be made, the particles chosen were those that seemed by eye to be nearest to cubes. To check the reproducibility of selection, and the validity of the use of the mean sieve size as an estimate of particle size, the selected particles were then weighed in groups of varying numbers, and the size/weight data obtained (Tables 4.1 to 4.10) were plotted logarithmically

TABLE 2

Coal Analyses

	PROXIMATE ANALYSIS 'AS RECEIVED'				ULTIMATE ANALYSIS Pure Coal (d.m.f.) Basis						
Name	Vol.	Moist.	Ash	CO_2	C	H	O	N	S	B.S. Swelling Number	Superficia Density g/c.c.
STANLLYD (Blanlnhirwaun)	7.9	1.3	2.9	0.73	93.00	3.35	1.59	1.33	0.73	n.c.	1.38
FIVE FT. (Deep Duffryn)	12.6	0.9	3.9	0.26	91.80	4.08	2.32	1.42	0.38	1	1.40
TWO FT. NINE	28.9	0.8	22.2	13.3	91.20	4.35	2.54	1.65	0.26	1	1.36
RED VEIN (Cilily)	20.5	1.0	1.6	0.04	89.70	4.66	3.55	1.67	0.42	6½	1.34
GARW (Cwm Tillery)	27.7	1.0	3.7	0.05	88.90	4.99	4.50	1.33	0.28	4	1.31
SILKSTONE (Elsecar)	39.6	1.3	1.7	0.35	86.90	5.79	5.50	1.51	0.30	4½	1.28
WINTER (Brimethorpe)	36.0	2.6	1.7	0.77	84.00	5.47	8.29	1.85	0.39	3	1.25
COWPEN (Northumberland)	34.6	7.3	4.1	0.95	82.70	5.40	9.60	1.80	0.50	1	1.27
HIGH HAZEL (Thorne)	36.7	5.1	1.0	0	81.90	5.57	10.52	1.58	0.43	1	1.27
LORRAINE (Faulquemont)	35.0	5.0	5.9	0.52	79.25	5.13	14.16	0.95	0.51	n.c.	1.36

TABLE 3

Sieve Fractions and their Mean Particle Size

Fraction Number	Mean Size Microns	Sieve Aperture	B.S. Sieve Number
		4.76 m.m.	3/16"
1	4060		
		3.35	5
2	3270		
		3.18	1/8"
3	3000		
		2.81	6
4	2610		
		2.41	7
5	2240		
		2.06	8
6	1870		
		1.68	10
7	1550		
		1.41	12
8	1310		
		1.20	14
9	1100		
		1.00	16
10	928		
		853	18
11	776		
		699	22
12	649		
		599	25
13	550		
		500	30
14	461		
		422	36
15	388		
		353	44
16	324		
		295	52

TABLE 4.1

Average Weight of Coal Particles (Stanllyd) (Microgm.)

Fraction no.	1	3	4	5	6	8	10	11	12	13	16
No. in group	3	3	3	5	5	5	10	10	15	15	20
Size: microns	4060	3000	2610	2240	1870	1310	928	776	649	550	324
I	55980	23150	16550	9940	5810	1540	625	325	190.0	110	25.0
II	53220	24320	17770	8790	5250	1870	660	325	163.3	120	22.5
III	52450	24450	16680	11220	6020	1660	640	360	173.3	110	25.0
IV	45830	23770	14420	10260	6640	1610	585	365	173.3	113	32.5
V	57200	24000	16080	9990	6150	1720	620	335	183.3	117	27.5
Average weight per fraction	52936	23938	16300	10040	5994	1680	626	342	176.6	110.6	26.5

TABLE 4.2

Average Weight of Coal Particles (Five ft.) (Microgm.)

Fraction no.	1	3	5	7	9	10	12	14	16
No. in group	3	3	5	5	10	10	15	15	20
Size: microns	4060	3000	2240	1550	1100	928	649	461	324
I	52230	22380	11320	3060	980	650	160.0	56.67	17.5
II	58550	23120	11120	3240	1035	685	173.3	60.00	15.0
III	60430	22130	10590	2540	1095	625	186.7	53.33	15.0
IV	61400	20900	9920	3240	1025	700	190.0	70.00	17.5
V	60820	21550	9590	3200	1030	565	180.0	70.00	20.0
Average weight per fraction	58686	22016	10508	3056	1033	645	198.0	62.00	17.0

TABLE 4.3

Average Weight of Coal Particles (Two ft. Nine) (Microgm.)

Fraction no.	1	4	7	10	13	16
No. in group	3	3	5	8	12	20
Size: microns	4060	2610	1550	928	550	324
I	64880	18470	4670	656.3	137.5	22.5
II	49280	19400	4200	693.8	125.0	22.5
III	63200	17020	4780	625.0	145.7	30.0
IV	82730	19630	3270	562.5	137.5	30.0
V	76770	15550	4820	637.5	108.3	22.5
Average weight per particle	67372	18014	4348	635.0	130.8	25.5

TABLE 4.4

Average Weight of Coal Particles (Red Vein) (Microgm.)

Fraction no.	1	4	7	9	10	13	15	16
No. in group	3	3	5	10	10	15	20	20
Size: microns	4060	2610	1550	1100	928	550	388	324
I	46270	16000	3100	900	590	93.33	50.0	10.0
II	46400	17600	2660	900	590	96.67	52.5	10.0
III	49700	17920	3130	1005	710	113.33	40.0	10.0
IV	45530	19350	3350	1045	670	123.33	42.5	30.0
V	50450	16650	3040	960	525	120.00	45.0	12.5
Average weight per fraction	47670	17504	3056	962	617	109.33	46.0	14.5

TABLE 4.5

Average Weight of Coal Particles (Garw) (Microgm.)

Fraction no.	1	3	6	8	10	13	16
No. in group	3	3	5	10	10	15	20
Size: microns	4060	3000	1870	1310	928	550	324
I	64520	21130	6150	1620	635	103.3	32.5
II	67230	23520	6020	1825	715	116.7	30.0
III	52880	21830	5180	2065	625	100.0	32.5
IV	60980	22750	5180	1755	675	130.0	30.0
V	61670	21550	5560	1880	705	103.3	27.5
Average weight per fraction	61460	22160	5618	1829	669	110.7	30.5

TABLE 4.6

Average Weight of Coal Particles (Silkstone) (Microgm.)

Fraction no.	1	3	6	9	11	12	14	16
No. in group	3	3	5	5	10	10	15	20
Size: microns	4060	3000	1870	1100	776	649	461	324
I	43580	25380	7060	1170	350	215	63.33	27.5
II	39280	24930	6130	1100	330	170	73.33	37.5
III	40150	25170	5640	1030	324	185	66.67	25.0
IV	39100	24430	5940	1020	330	225	86.67	20.0
V	39600	25430	470	1090	350	165	83.33	27.5
Average weight per fraction	40342	25070	5899	1082	337	192	74.67	25.5

TABLE 4.7

Average Weight of Coal Particles (Winter) (Microgm.)

Fraction no.	1	3	6	9	11	14	16
No. in group	3	3	5	5	10	15	20
Size: microns	4060	3000	1870	1100	776	461	324
I	49820	25200	6500	1040	360	70	20
II	48170	23400	5120	870	290	96.7	22.5
III	53450	24400	5830	1090	400	80	20
IV	49280	23950	5410	1180	420	83.3	27.5
V	53520	27400	4210	1150	320	73.3	22.5
Average weight per fraction	50850	24870	5414	1066	358	80.7	22.5

TABLE 4.8

Average Weight of Coal Particles (Cowpen) (Microgm.)

Fraction no.	1	3	6	9	11	13	16
No. in group	3	3	5	5	10	15	20
Size: microns	4060	3000	1870	1100	776	550	324
I	62880	23900	5080	1130	390	106.7	20.0
II	50830	24980	5370	990	410	96.7	20.0
III	52720	23520	6430	1000	385	106.7	20.0
IV	63370	24950	5640	1130	395	96.7	20.0
V	53720	26800	5750	1070	395	110	17.5
Average weight per fraction	56700	24780	5654	1064	395	103.4	19.5

TABLE 4.9

Average Weight of Coal Particles (High Hazel)

Fraction no.	No. in group	Size: microns	Weight: microgm.
1	5	4060	65040
2	5	3270	27540
3	5	3000	26920
4	5	2610	15720
5	5	2240	10000
6	5	1870	5300
7	5	1550	2940
8	5	1310	1480
9	20	1100	1130
10	20	928	540
11	20	776	390
12	30	649	223
13	40	550	140
14	50	461	70
15	60	388	43.3
16	70	324	24.3

TABLE 4.10

Average Weight of Coal Particles (Lorraine) (Microgm.)

Fraction no.	1	3	6	9	11	14	16
No. in group	4	4	4	10	10	15	20
Size: microns	4000	3000	1870	1100	776	461	324
I	78440	23960	5740	1060	380	83.3	37.5
II	79500	26200	5760	985	375	73.3	30.0
III	78700	26120	5760	1015	370	86.7	27.5
IV	84960	20580	6700	1005	455	86.7	30.0
Average weight per fraction	80400	24215	5990	1015	395	82.25	31.25

(Figs. 4.1 to 4.10). These graphs obey the empirical equation

$$w_o = M.d_o^{\ m} \qquad (2)$$

where w_o and d_o are initial weight and diameter of the particles; M and m are empirical constants whose values, determined from the graphs, are given in Table 5.

Of the 300 odd particles of each coal selected for weighing about 120 were then selected for mounting and burning; the actual numbers are listed in Table 6. The mounting of the particles on the silica threads was done by getting a small blob of cement on the end of the thread and leaving this in contact with the particle for a few minutes. This was always done the day before the particles were burned to allow the cement to dry out, since tests showed that, on burning the particle the same day, the cement would swell as it lost moisture, and reflection of radiation from the coils by the swelling cement sometimes generated a spurious "burning" trace; also the particles were liable to drop off as the cement set. At the other extreme, if the particles were left too long the cement seemed to become brittle and to crack under the heat so that again the particles were liable to drop off.

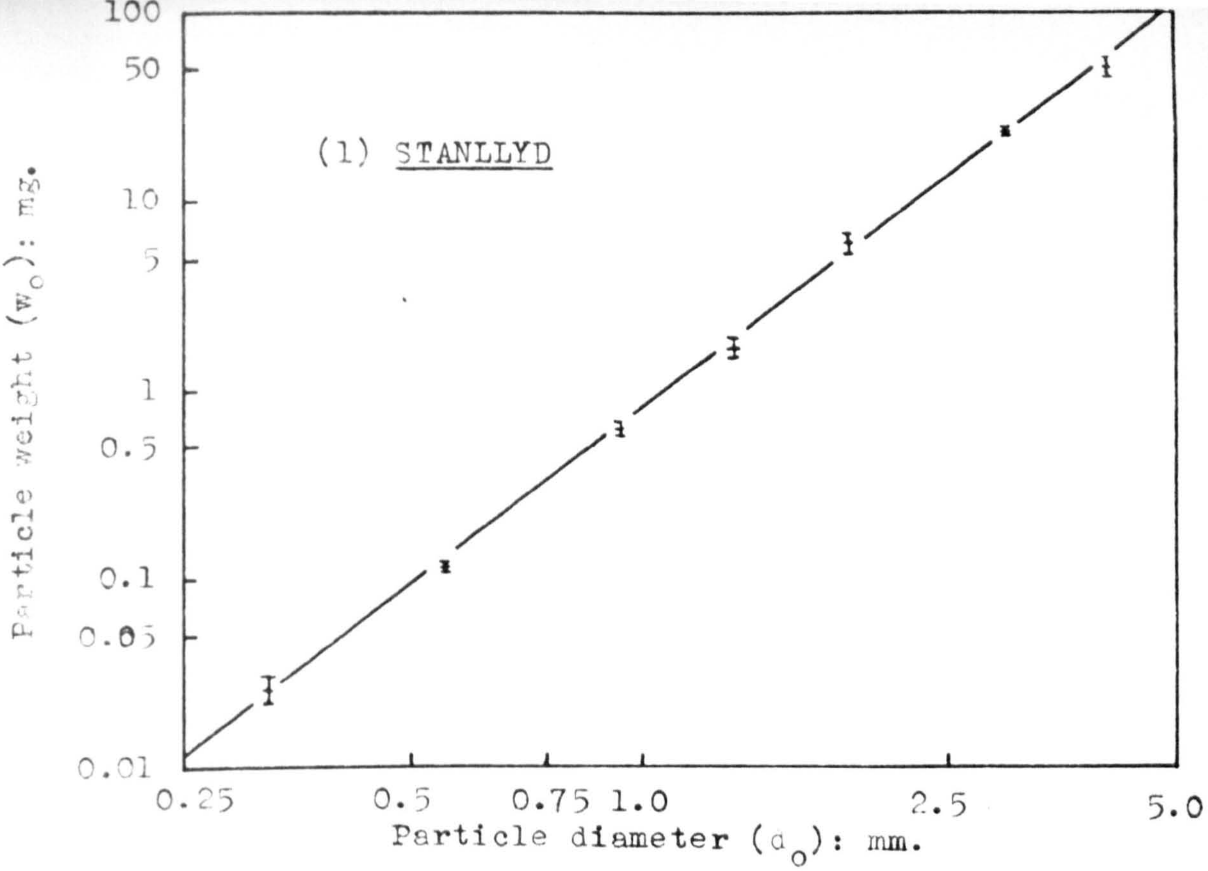


Fig. 4.1 - Variation of particle weight with particle diameter.

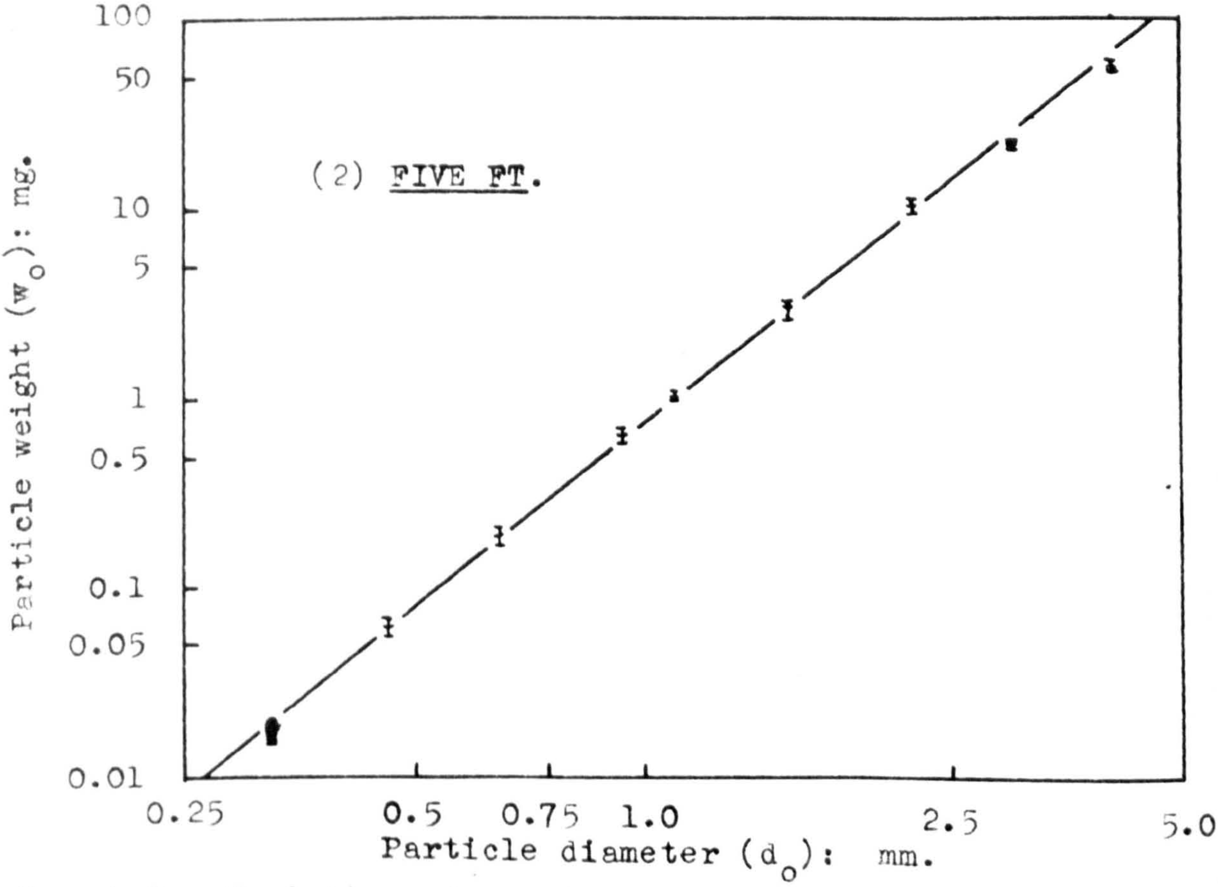


Fig. 4.2 - Variation of particle weight with particle diameter.

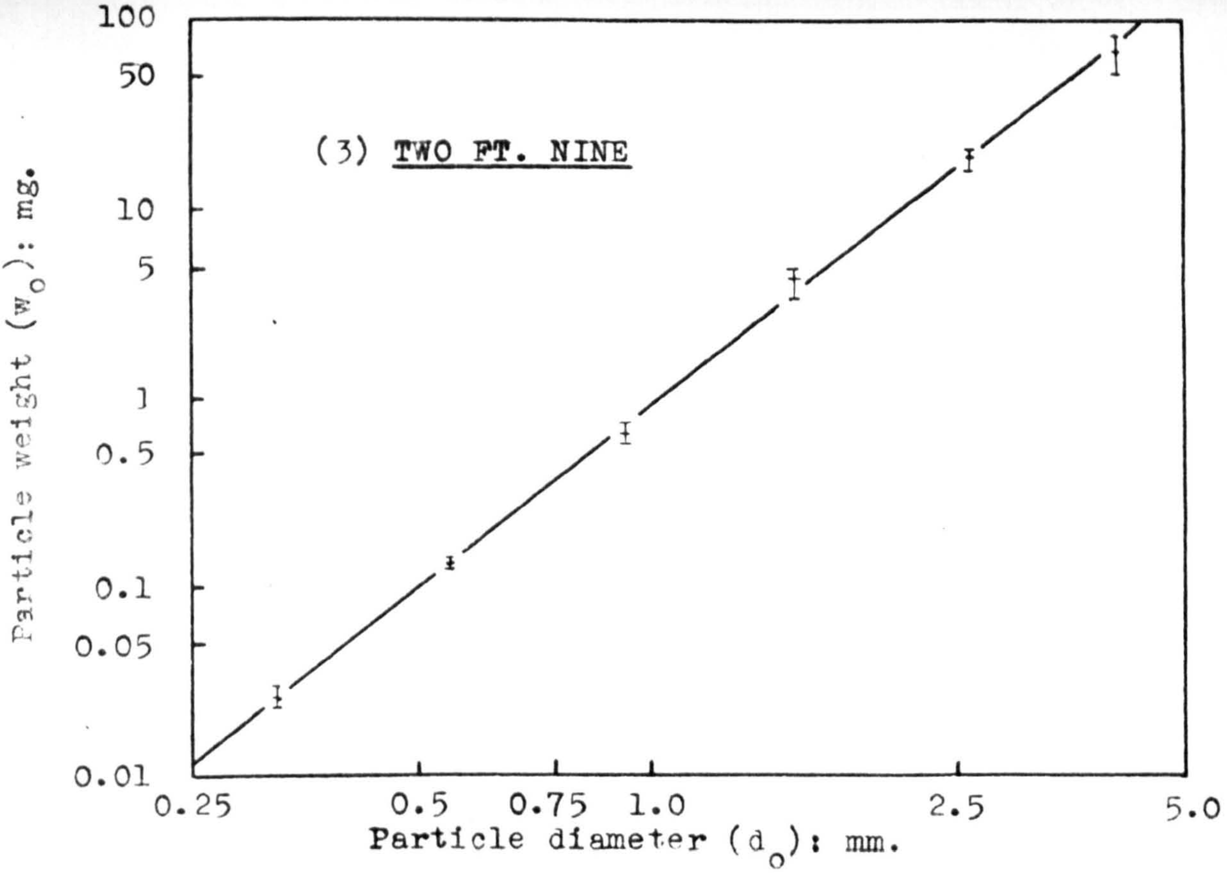


Fig. 4.3 - Variation of particle weight with particle diameter.

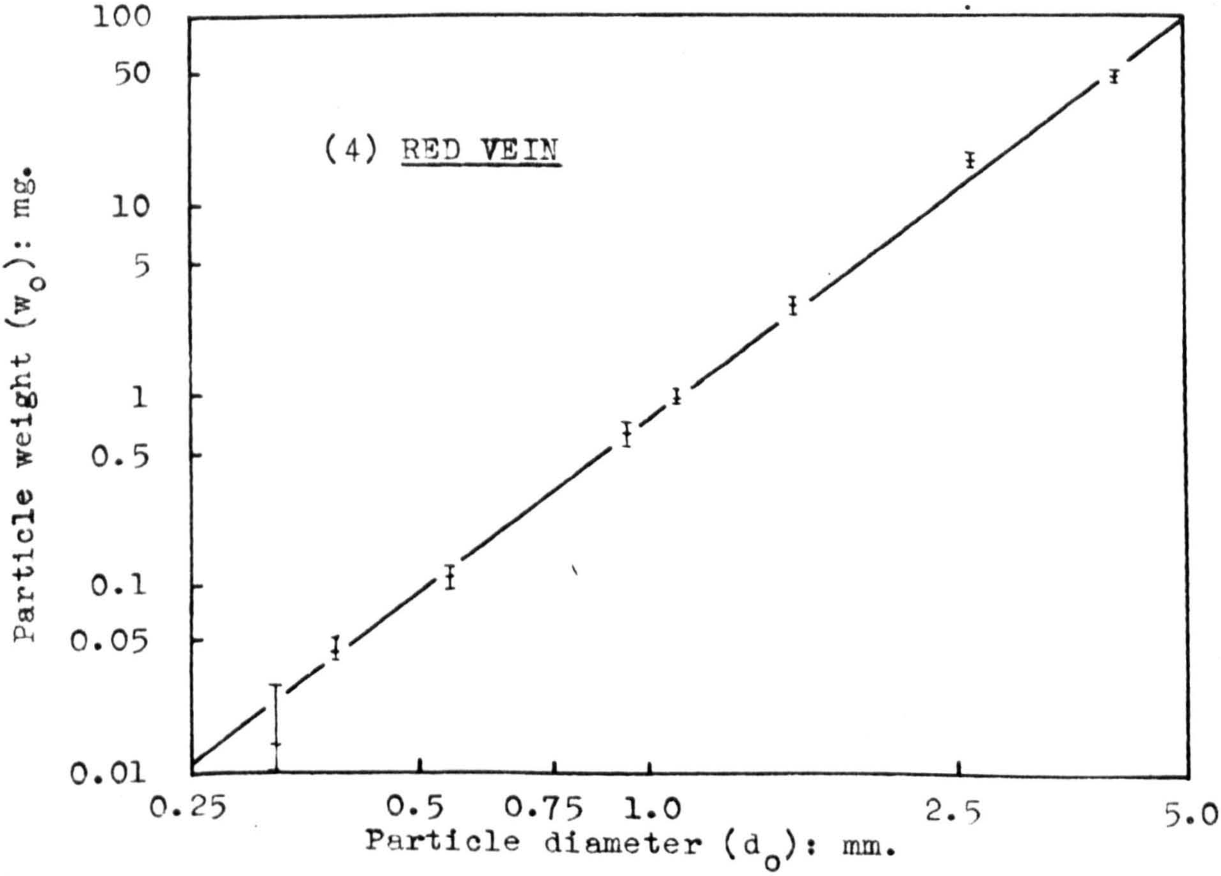


Fig. 4.4 - Variation of particle weight with particle diameter.

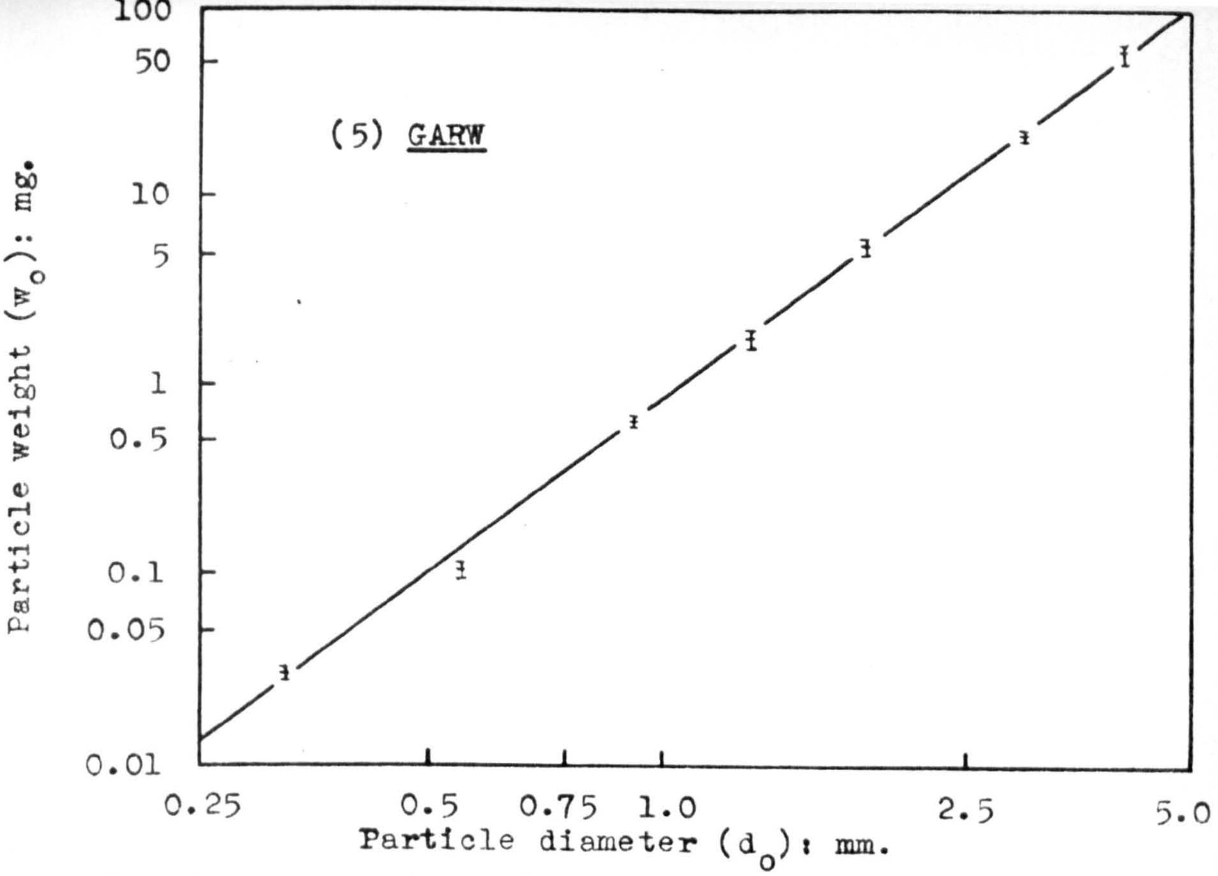


Fig. 4.5 - Variation of particle weight with particle diameter.

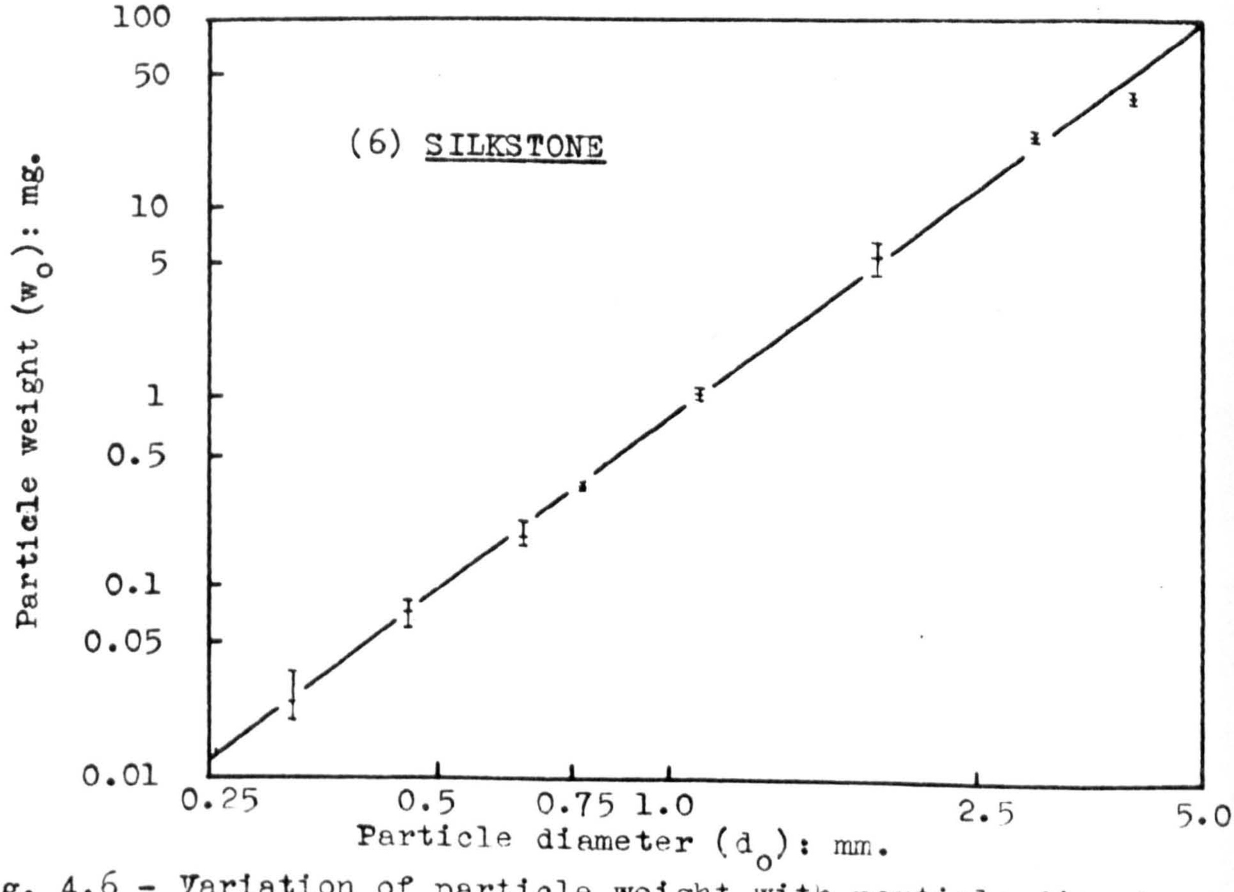


Fig. 4.6 - Variation of particle weight with particle diameter.

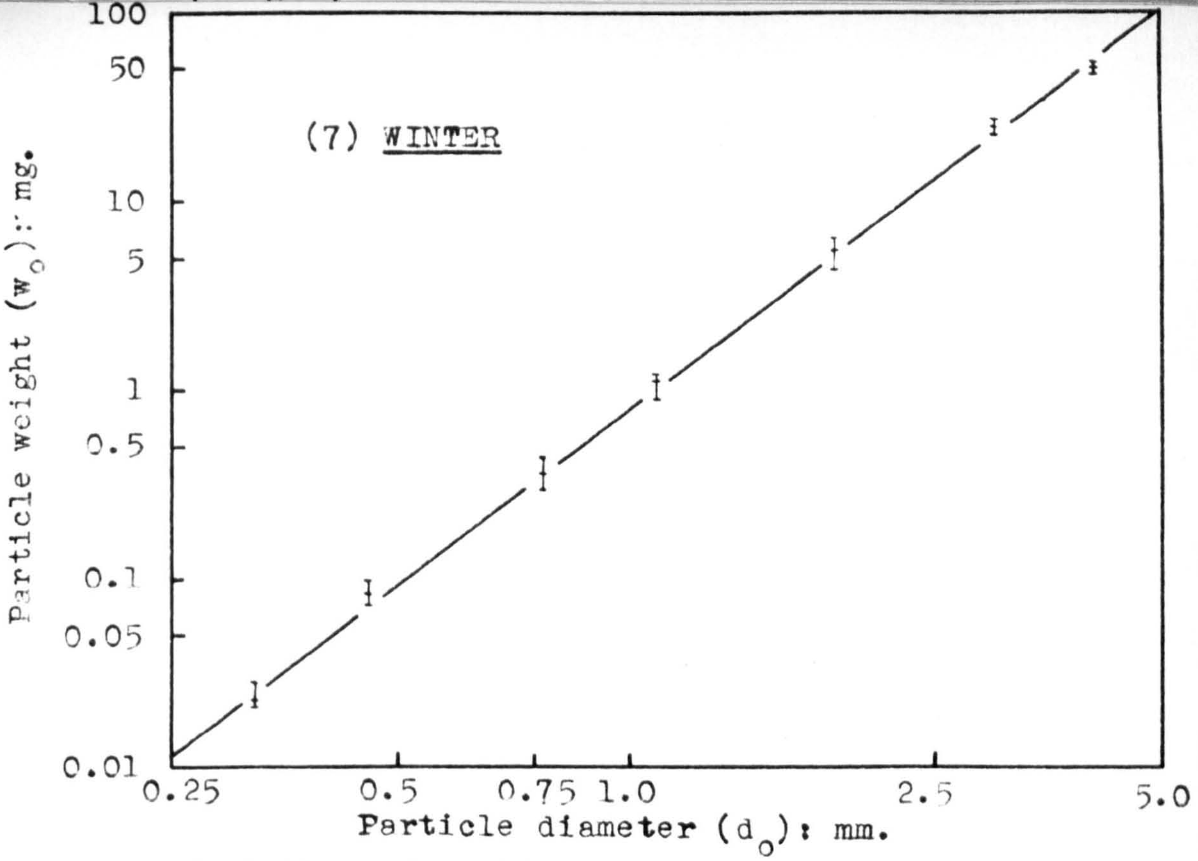


Fig. 4.7 - Variation of particle weight with particle diameter.

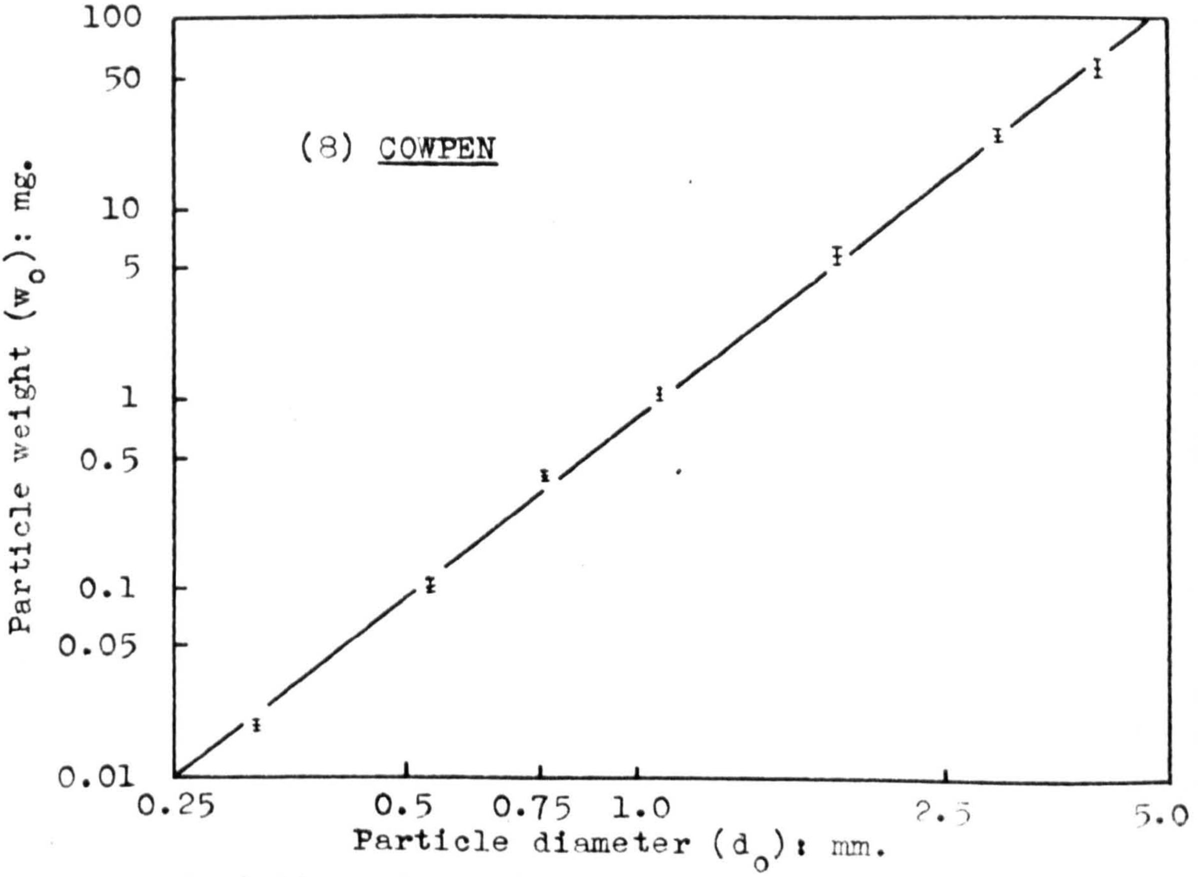


Fig. 4.8 - Variation of particle weight with particle diameter.

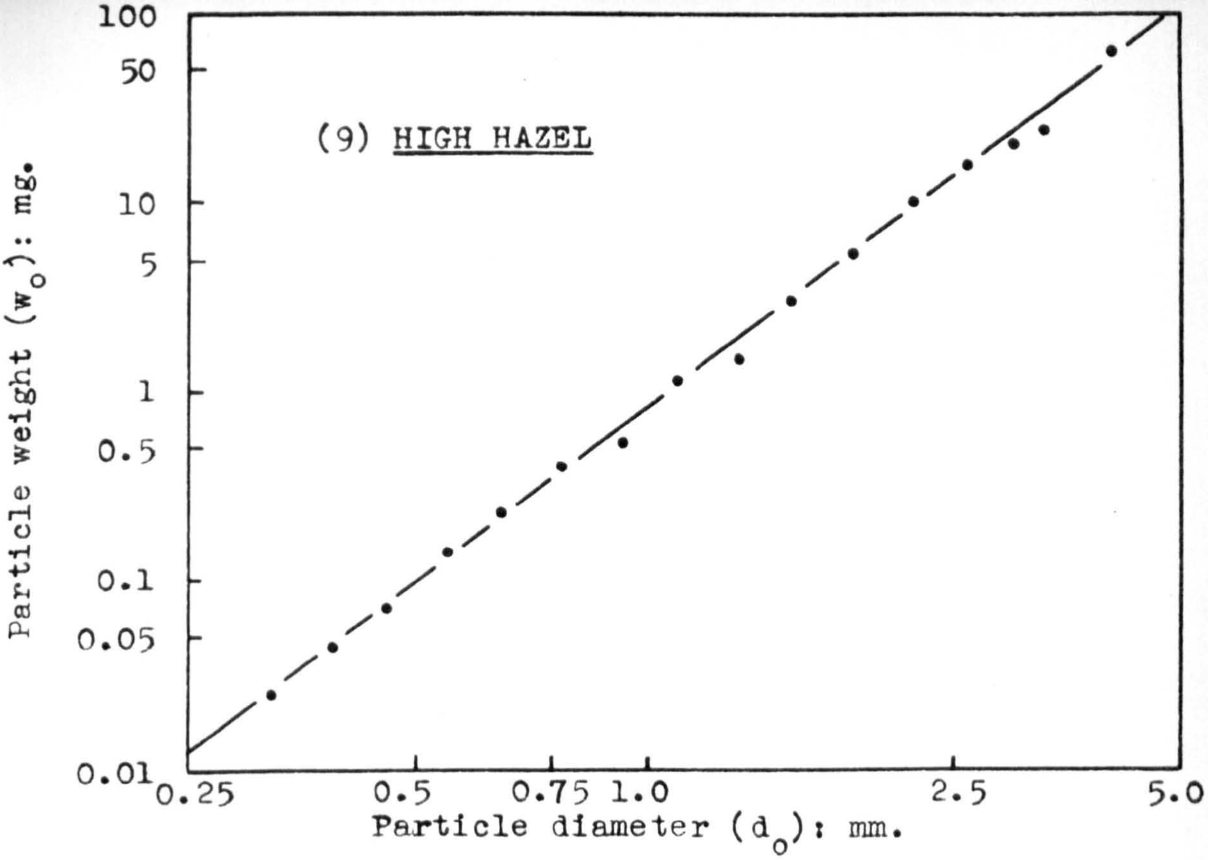


Fig. 4.9 - Variation of particle weight with particle diameter.

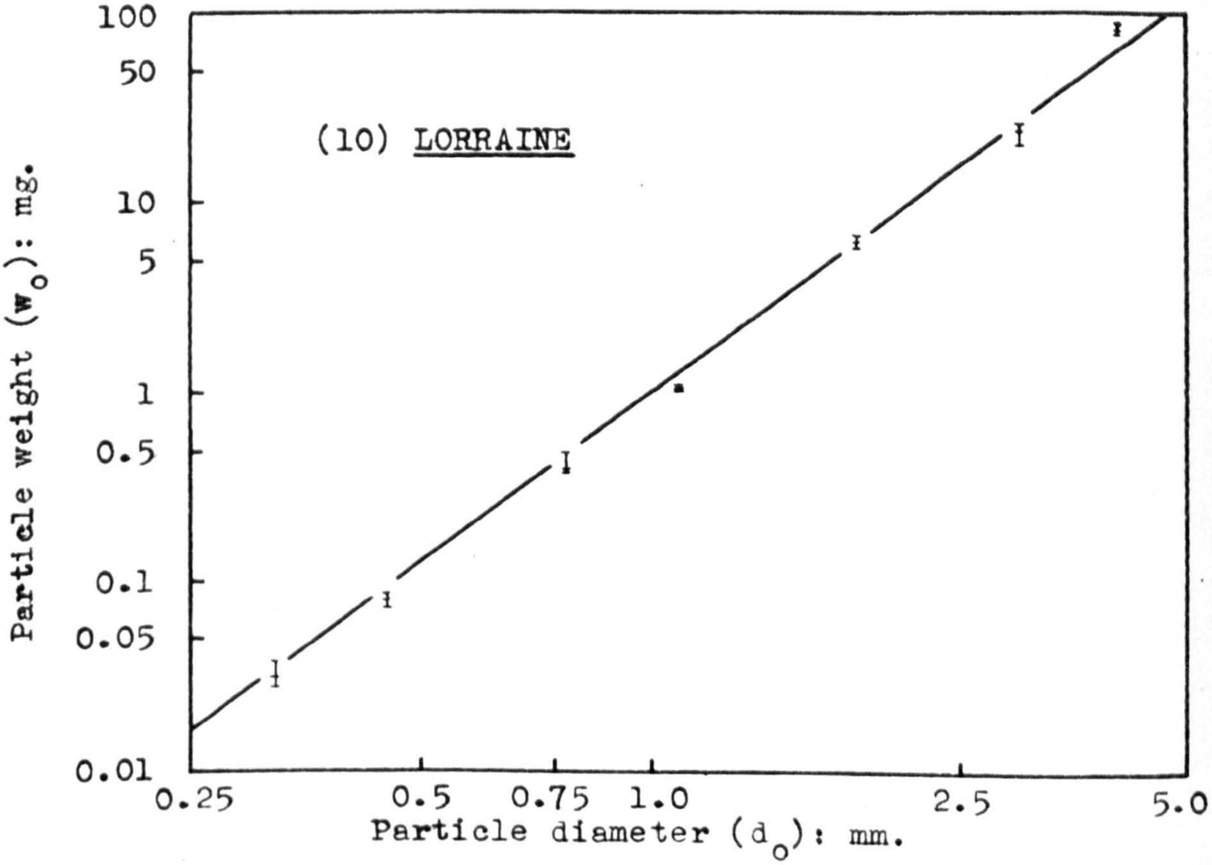


Fig. 4.10 - Variation of particle weight with particle diameter.

TABLE 6

Numbers of Particles Selected from Each Size Fraction for Weighing[x] and Burning

		(1) Stanllyd	(2) Five ft.	(3) Two ft. Nine	(4) Red Vein	(5) Garw	(6) Silkstone	(7) Winter	(8) Cowpen	(9) High Hazel	(10) Lorrai
Carbon percentage (d.m.f.)		93.0	91.8	91.2	89.7	88.9	86.9	84.0	82.7	81.9	79.3
	Size (μ)										
1	4060	3(5)	3(5)	3(5)	3(5)	3(5)	3(5)	3(5)	3(5)	5(1)	4(4)
2	3270	-	-	-	-	-	-	-	-	5(1)	-
3	3000	3(5)	3(5)	-	-	3(5)	3(5)	3(5)	3(5)	5(1)	4(4)
4	2610	3(5)	-	3(5)	3(5)	-	-	-	-	5(1)	-
5	2240	5(5)	5(5)	-	-	-	-	-	-	5(1)	-
6	1870	5(5)	-	-	-	5(5)	5(5)	5(5)	5(5)	5(1)	4(4)
7	1550	-	5(5)	5(5)	5(5)	-	-	-	-	5(1)	-
8	1310	5(5)	-	-	-	10(5)	-	-	-	5(1)	-
9	1100	-	10(5)	-	10(5)	-	5(5)	5(5)	5(5)	20(1)	10(4)
10	928	10(5)	10(5)	8(5)	10(5)	10(5)	-	-	-	20(1)	-
11	776	10(5)	-	-	-	-	10(5)	10(5)	10(5)	20(1)	10(4)
12	649	15(5)	15(5)	-	-	-	10(5)	-	-	30(1)	-
13	550	15(5)	-	12(5)	15(5)	15(5)	-	-	15(5)	40(1)	-
14	461	-	15(5)	-	-	-	15(5)	15(5)	-	50(1)	15(4)
15	388	-	-	-	20(5)	-	-	-	-	60(1)	-
16	324	20(5)	20(5)	20(5)	20(5)	20(5)	20(5)	20(5)	20(5)	70(1)	20(4)
Nos. selected for weighing (Total: 3498)		470	430	255	430	330	355	305	305	350	268
Order of Burning the coals		(7)	(8)	(3)	(4)	(9)	(6)	(5)	(10)	(1)	(2)
Nos. selected for burning		190	180	100	135	120	120	120	120	136	112

[x] First number is number of particles in group;
Second number (in brackets) is number of groups.

4.3 Experimental Procedure - When the coal to be burned had been crushed and sieved, and the selected particles had been weighed, the particles selected for burning were then mounted on their silica fibres and stacked upright in a rack ready for burning the following day. In the case of High Hazel coal, which was the first coal to be examined, particles from only one or two sieve cuts were dealt with at a time so that the results for all the sieve cuts were obtained over a period of a month or so. After that, with the satisfactory development of the necessary technique, each one of the other coals was dealt with in a single day, or at most two, with only one day in between for mounting a second set of particles.

The racks in which the particles were stacked were made out of two squares of wire gauze roughly 4" x 4", clamped horizontally about 1/2" apart with the lower gauze about 1/2" above a base plate. To carry out an experiment a mounted particle was clamped in position between the heating coils and so adjusted that by eye it appeared to be midway between the coils. To hold the particle in position, the silica fibre was inserted into a glass capillary tube about 1" long that had a kink in it so that it gripped the stem of the silica fibre quite firmly; the capillary tube itself was mounted in a cork so that it could be firmly held in a quick release clip

that was mounted on a fully adjustable swivel.
When the particle was in position the recorder chart was started and simultaneously the current to the heating coils was switched on. The coils then heated up and the particle eventually burst into flame. After it had burnt out the various units were switched off, a new particle set in position and the experiment was repeated.

5. THEORY

In this section it is not my intention to develop a new theory but only to outline the current theory to explain the objectives of the present work, and to provide a basis for certain comparisons to be made in a later section.

5.1 Theory of Reaction Control by Diffusion

5.1.1 Basic postulates - The current theory of particulate combustion is based on the diffusion theory of reaction control (5 - 12). On this theory the coal particle, or the solid residue remaining after devolatilization, is regarded for the purpose as being equivalent to a pure carbon sphere that is consumed by reaction with oxygen which must reach the solid surface only after traversing a boundary layer of reaction products. The diffusion system has three main components: oxygen, reaction products and nitrogen; but since the concentration of reaction products is small (when combustion takes place in air) these are generally disregarded compared with the nitrogen as a resistive factor to the transport of the oxygen. This conveniently reduces the system to two components: oxygen diffusing through stationary nitrogen, and this simplifies the mathematics considerably.

If the particle is also subject to an aerodynamic field, the immensely complex motion of the real fluid system is replaced in theory by a much simplified equivalent system of a spherically symmetrical boundary film having the following properties: outside the film, turbulence and other mixing factors are assumed to destroy all concentration gradients so that the main stream concentration of oxygen is uniform; inside the film, mass transfer is assumed to take place only radially and only by molecular diffusion, all other macroscopic motion of the fluid being assumed negligible; finally, the thickness of the diffusion layer (denoted by δ) is assumed to be controlled by the external aerodynamics of the system, and not in any way by the diffusion process itself, and is also assumed to have a value having some physical reality at a first order of magnitude.

5.1.2 Basic equations - The reaction rate, and hence the burning time, may now be determined by calculating the rate of diffusion of oxygen to the solid surface, since if R_s is the specific reaction rate (mass per unit area per sec) and G_s is the rate of oxygen transfer to unit area of the solid surface

$$R_s \propto G_s \tag{3}$$

The rate of mass transfer by molecular diffusion can be calculated from Ficks law that, in spherically symmetrical polars, can be written for the steady state condition

$$G = -D.\frac{dN}{dr} + v.N \tag{4}$$

where D is the diffusion coefficient; r is the radial distance from the centre of the particle; N is the oxygen concentration in <u>number of molecules</u> per unit volume; and v is the velocity of the diffusional convective flow.

To calculate G from equation (4), N must first be determined as a function of r from the second order form of Ficks equation. For the steady state this may be written, in spherically symmetrical polars

$$\frac{d^2N}{dr^2} + \left[\frac{2}{r} + \frac{a^2}{L_s.r^2}\right] \cdot \frac{dN}{dr} = 0 \tag{5}$$

where L_s is a characteristic length defined by

$$L_s = -D/v_s \tag{6}$$

and v_s is the velocity of the convective flow at the solid surface (i.e. at r = a) so that

$$v_s.a^2 = v.r^2$$

The full solution to equation (5) can be written in the convenient form

$$\frac{N - N_o}{N_s - N_o} = \frac{\Delta N}{\Delta N_o} = \frac{\exp(-a^2/\delta L_s) - \exp(-a^2/rL_s)}{\exp(-a^2/\delta L_s) - \exp(-a / L_s)} \tag{7}$$

where the subscripts s and o refer to surface and main stream concentrations respectively (i.e. at $r = a$, and $r = \delta$).

For the special conditions that $\delta = \infty$ (i.e. no velocity field), and $N_s = 0$ (i.e. immediate reaction at the solid surface), equation (7) can be written in the approximate - and more familiar - form, after expanding the exponentials to their second term

$$N/N_o = p/p_o = 1 - a/r \qquad (8)$$

where p is the oxygen partial pressure. Equation (8) is illustrated graphically in Fig.5.

5.1.3 <u>Rate equations</u> - with the above equations we may now deduce the relation for the reaction rate. Differentiating N in equation (7) with respect to r and substituting in equation (4) for $r = a$ we get

$$G_s = \frac{MD}{a(1 - a/\delta)} \cdot \ln \left[1 - \frac{\Delta N_o}{M - N_s} \right] \qquad (9)$$

where M is the total number of molecules of all species. When ΔN_o is small compared with M, which is the case for oxygen in air, the logarithmic term may be replaced by the first term of its expansion, so equation (9) reduces to

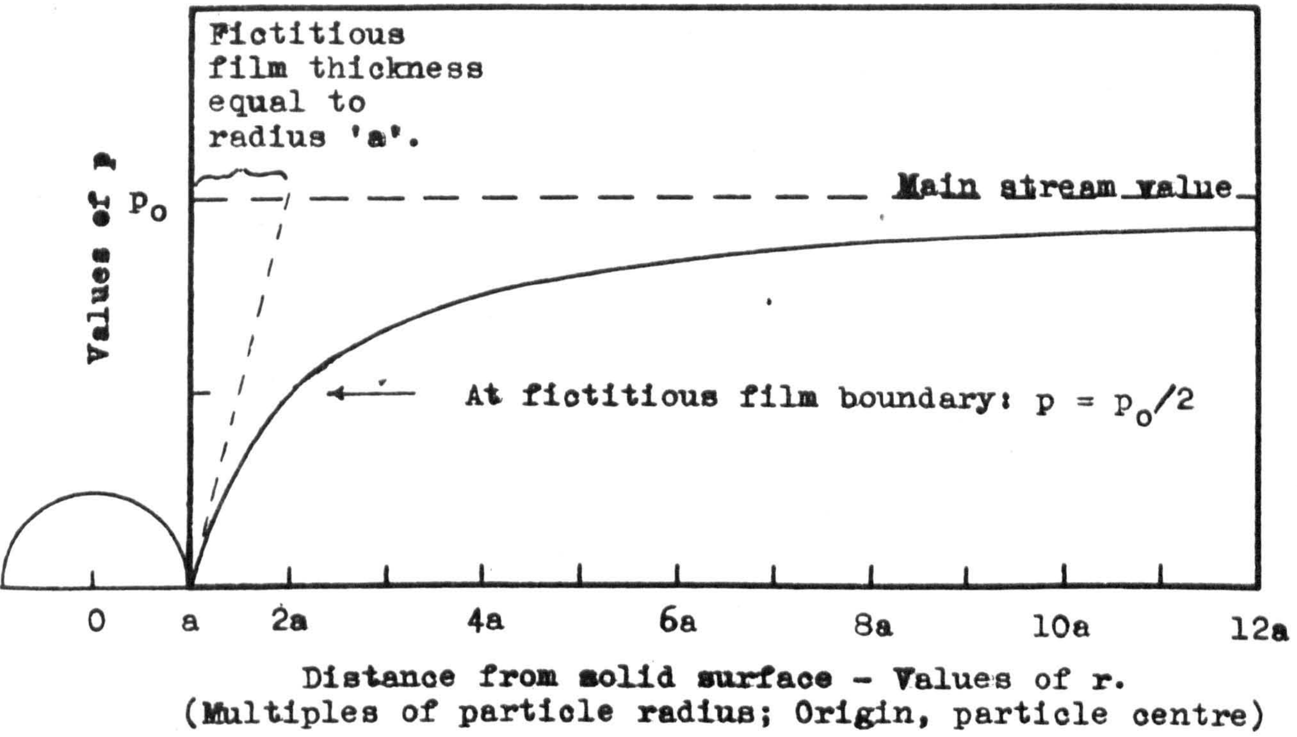


Fig. 5 - Variation of oxygen partial pressure (p) with distance from the surface of a solid spherical particle (of radius a); the curve obeys equation (8):

$$p = p_o(1 - a/r)$$

This diagram illustrates the relationship between the physical thickness and the fictitious thickness of the mass-transfer boundary layer, the fictitious film thickness being given by the intercept, on the line at $p = p_o$, generated by the slope to the curve at the solid surface.

$$G_s = D.\frac{\Delta N_o}{a}\cdot\frac{1}{(1 - a/\delta)(1 - N_s/M)} \qquad (10a)$$

$$= D.(N_o/a) \quad \text{when } \delta = \infty \text{ and } N_s = 0 \qquad (10b)$$

Equations (8) and (10b) can be used to illustrate a dimensional point that becomes of special significance with reference to flames (see sec.7), but it is also important with single particles. Equation (8), as illustrated in Fig.5, shows N (or p) rising from zero at the solid surface ($r = a$) to N_o (or p_o) at $r = o$. The slope of the curve at $r = a$ gives an intercept on the line $p = p_o$ at $r = 2a$, so that the slope of that line is N_o/a. Since this is the value of the slope that is required to give equation (10b) direct from equation (4) when v is small, this intercept is sometimes referred to as the effective or fictitious boundary film thickness. It should not be forgotten however that at $r = 2a$, $N = N_o/2$; that is to say, that the effective film thickness is much less than the physical thickness. If this latter is taken arbitrarily as the point $p = 99\% p_o$

$$\text{then } \delta_{(\text{physical})} = 100.a = 100.\delta_{(\text{effective})}.$$

In passing, we may note that, in the equations for a flat plate instead of a sphere, the characteristic length L defined by equation (6) also appears and can be identified for that system as the effective film thickness defined by the same intercept method.

5.1.4 Burning times - In deriving the burning time equation, the special case that $\delta = \infty$ and $N_s = 0$ will be taken. From equations (3) and (10a), and inserting the appropriate constants in a convenient form, we may write

$$R_s = -\sigma.\frac{da}{dt} \quad \text{by definition} \qquad (11a)$$

$$= \frac{\sigma}{8K_D}\cdot\frac{1}{a} \quad \text{by transformation of equation (10a)} \qquad (11b)$$

where σ is the density of the solid, and K_D is the theoretical burning constant given by

$$K_D = \frac{\sigma}{3\rho_o D_o p_o (T/T_o)^{0.75}} \qquad (12)$$

where ρ = density of air at N.T.P. = 1.29×10^{-3} g/cc
D_o = diffusion coefficient of O_2 in N_2 = 0.181 sq. cm./sec
p_o = main stream fractional oxygen partial pressure = 0.21
T = absolute temperature of reaction; $T_o = 273^\circ$ K

Integration of the rate equation above, between the limits $a = d_o/2$ at $t = 0$, and $a = 0$ at $t = t_b$, gives the burning time equation

$$t_b = K_D . d_o^{\,2} \qquad (1)$$

5.1.5 Assumptions of diffusion theory - Some of the assumptions involved in deriving the equation above have already been explicitly stated; there are also others, and in assessing the validity of this equation it is desirable to have all the assumptions listed. These are:

(i) that the coal particle approximates to a carbon sphere, though a correction for the volatile loss can (and will) be made.

(ii) that the equivalent spherical particle burns uniformly from the outside without swelling (47) or internal burning (63,27). Swelling can be corrected for if the degree of swelling is known; but internal burning is particularly difficult to correct for as its existence tends to contradict the diffusion hypothesis (64).

(iii) that in a velocity field the particle is surrounded by a spherically symmetrical boundary layer that is stagnant save for molecular motion.

(iv) that steady state conditions are quickly established and are then maintained. Only exact calculations (e.g. by numerical solution of the time variable equations) can show the validity of this assumption, and at present the labour required is not thought to be justified in view of the influence of the other assumptions involved.

(v) that the effective system involves two gases only: oxygen diffusing through stationary nitrogen; and that the influence of the reaction products can be neglected. When the combustion gas is air this is reasonable.

(vi) that reaction is solely at the solid surface with none in the gas phase inside the boundary layer.

(vii) that the oxygen concentration at the solid surface is negligible or zero. Because chemisorption of oxygen on carbon is activated, the surface concentration of oxygen is never zero though it may be negligible.

5.2 Theory of the Chemical Rate Control - If the surface oxygen concentration is not negligible the equations for the reaction rate and the burning time are considerably modified. We again adopt the assumptions that the coal particle is equivalent to a carbon sphere burning uniformly at the outside surface only. In the limiting case, with no effective boundary layer whatever, the oxygen partial pressure has the main stream value p_o. The specific reaction rate is then constant with respect to particle size, being a function of temperature and oxygen concentration only, and given by

$$R_s = -\sigma . \frac{da}{dt} = -kp_o \qquad (13)$$

where k is the temperature-dependent constant of proportionality. Integrating between the limits

$$a = d_o/2 \text{ at } t = 0$$
$$\text{and } a = 0 \quad \text{at } t = t_b \text{, gives}$$

$$t_b = \frac{\sigma}{2kp_o} . d_o = K_c . d_o \qquad (14)$$

From kinetic theory, K_c is given by

$$K_c = \frac{4\sigma}{3}\left(\frac{2\pi RT}{M_o}\right)^{1/2} \cdot \frac{1}{p_o \cdot \exp(-E/RT)} \qquad (15)$$

where σ, p_o and T are as previously defined; R is the gas constant; E is the activation energy of the reaction system = 4000 cal. (65); and M_o is the mean molecular weight of the gas mixture.

Comparison of equations (11) with (13), and of (1) with (14) show that these pairs differ by one power of the diameter, so that if one or other mechanism dominates the reaction, the relevant power of the diameter (measured experimentally) should be near a whole number; but if both mechanisms are of the same order of magnitude then the relevant power of the diameter should lie between two whole numbers: between - 1 and 0 in the rate equations, and between 1 and 2 for the burning time equations. This should therefore provide a fairly sensitive test of the relative importance of the two mechanisms.

6. RESULTS

6.1 General Characteristics of Combustion - Combustion of the particles under the influence of the heating coils had three stages: heat up to ignition; volatile combustion; and residue combustion. As the coils heated up the particle temperature rose but with a lag of some 300 or 400° C. This lag was discovered by drilling a few particles and inserting a thermocouple. By the time the coils were glowing red the particles had usually started to smoke a bit and then shortly, if they were large enough, the volatiles would burst into flame to burn in their characteristic flickering manner. When this had ceased there was usually a slight but noticable pause and then the residue glowed red and started to burn out; sometimes a combustion wave could be seen spreading slowly over the black residue. The start of the residue combustion was often preceded by a sudden intense glow round the particle that quickly flashed up and as quickly died away to the faint but clearly seen glow of CO combustion in a thin film round the particle. The particle temperature reached its maximum just after the residue had started to burn and then declined slowly but steadily. The end of the residue combustion was always quite clear to the eye except in one or two instances with the heavy-ash Two ft. Nine coal when it would appear that a random variation in local ash concentration had increased this to the point where the signal from the combustion was drowned by the background signal of light reflected from the ash.

The burning particles thus showed the well known phenomena of volatile combustion followed by residue combustion, and, fortunately, the irregular trace obtained on the pen recorder from the flickering volatile flame could be clearly differentiated from the more regular trace obtained from the residue reaction. These characteristics are clearly seen in Fig.6, which is a typical record obtained (Winter coal, particle size 3 mm.).

The differentiation in the two traces is emphasised by a drop in the radiation intensity that marks the pause mentioned above between the finish of the volatile flame and the start of the residue combustion. This phenomenon, which always occurred had previously been indicated by Orning (25).

6.2 Combustion of the Volatiles - The values of volatile burning time obtained are given in Tables 7.1 to 7.10. Few results were obtained from the smaller particles since the volume of volatiles generated by these was too small to provide an inflammable mixture. Of 1300 particles mounted for burning, 650 generated measurable traces of volatile burning time.

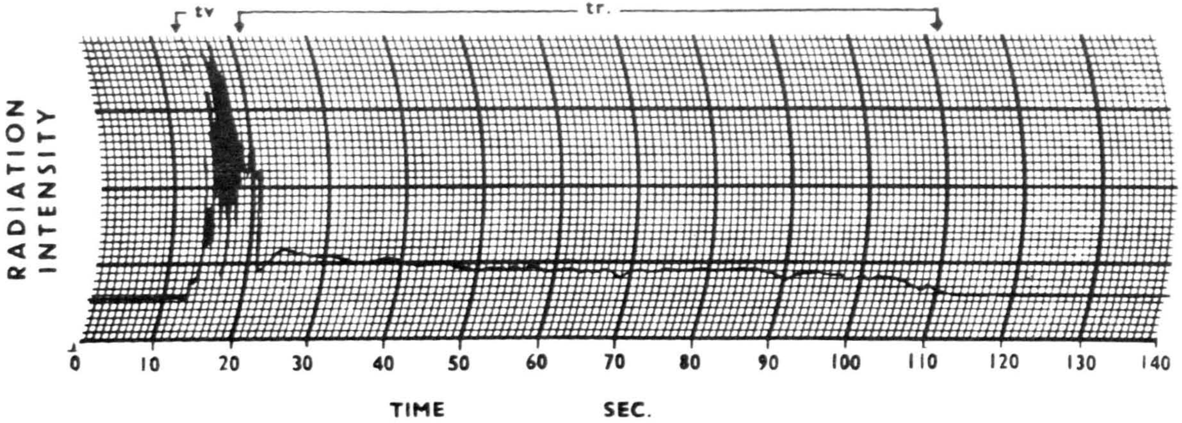


Fig. 6 - Pen recorder trace of radiation from burning particle.

Winter coal (particle I3): size 3 mm; weight 23.95 mg.
Volatile burning time (t_v): 8 sec.
Residue burning time (t_r): 90 sec.

TABLE 7.1

Volatile Burning Times (Stanllyd)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	55980	7	10	11
	53220	8	9	7
	52450	7.5	10	8
	45830	7	8	7
	57200	10	12	9
(3) 3000	23150	5	4	-
	24320	5	5.5	-
	24450	5	4	5
	23770	5	5	6
	24000	6	5	5
(4) 2610	16550	5	4	3.5
	17770	4	4	4
	16680	4	5	4
	14420	3	4.5	3.5
	16080	4	4	4.5
(5) 2240	9940	3.5	2.5	3
	8790	2.5	2.5	3
	11220	3	3	4
	10260	2	4	4
	9990	3	4	3
(6) 1870	5810	3	2	2
	5250	2.5	2.5	2
	6020	3	2	2
	6640	3	-	-
	6150	2.5	3	-
(8) 1310	1540	-	1.0	0.8
	1870	1.1	1.4	1.2
	1660	1.0	1.0	1.2
	1610	1.2	1.2	1.0
	1720	0.8	-	-

TABLE 7.2

Volatile Burning Times (Five ft.)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)		
		1	2	3
(1)	52230	-	9.5	6
4060	58550	9	9.5	8
	60430	10.5	12.5	11
	61400	10	10	11.5
	60820	7	8	11
(3)	22380	7	6	5
3000	23120	5	5	7
	22130	6	5.5	5.5
	20900	7	8	5
	21550	6.5	7	6.5
(5)	11320	2	3	3
2240	11120	3.5	3	3.5
	10590	3	3.5	-
	9920	3	-	3.5
	9590	3	3	2
(7)	3060	1.6	1.3	1.5
1550	3240	1.4	1.5	1.8
	2540	1.8	0.8	1.5
	3240	1.6	2.2	1.2
	3200	-	1.2	1.6
(9)	980	-	-	0.5
1100	1095	-	0.4	-
	1030	-	0.4	0.4
(10)	650	0.3	-	-
928	565	0.3	-	-

TABLE 7.3

Volatile Burning Times (Two ft. Nine)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	64880	-	-	14
	49280	7	-	12
	63200	11	13	11
	82730	14	12	12.5
	76770	-	-	11
(4) 2610	18470	5	4	6
	19400	4	5	-
	17020	5	3.5	5
	19630	5	4.0	5
	15550	4	5.5	5
(7) 1550	4670	1.0	-	1.1
	4200	1.1	0.9	0.8
	3270	-	1.6	-
	4820	-	1.2	1.0
(10) 928	656.3	-	0.2	0.3
	625.0	-	0.35	0.2
	562.5	-	0.30	-

TABLE 7.4

Volatile Burning Times (Red Vein)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	46270	9.5	11.5	12
	46400	9.5	-	11.5
	49700	12.5	13.5	11
	45530	12	-	8.5
	50450	12.0	12.0	-
(4) 2610	16000	5.5	-	7
	17600	5.5	7	8
	17920	6	6.5	7
	19350	6	6	5
	16650	6.5	4	4.5
(7) 1550	3100	1.4	1.4	1.4
	2660	1.0	2.2	0.9
	3130	1.9	1.0	1.6
	3350	1.3	1.2	1.6
	3040	1.0	1.5	1.1
(9) 1100	900	0.6	0.7	0.5
	900	0.4	0.7	0.8
	1005	0.4	0.7	1.1
	1045	0.7	0.8	0.35
	960	0.8	0.8	0.8
(10) 928	590	0.6	0.7	0.5
	710	0.6	-	0.5
	670	0.4	0.6	-
	525	-	-	0.8

TABLE 7.5

Volatile Burning Times (Garw)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	64520	17	17.5	14	
	67230	16	17	19	
	52880	15	18	12	
	60980	17	16.5	16	
	61670	19	16	18	
(3) 3000	21130	9.5	6.5	9	
	23520	7	8.5	8.5	
	21830	8	8	7	
	22750	8	9	7	
	21550	7.5	8.5	7.5	
(6) 1870	6150	3.1	3.1	3.5	
	6020	3.4	3.6	3.6	
	5180	3.0	3.4	3.4	
	5180	2.8	3.6	3.2	
	5560	3.6	3.0	3.8	
(8) 1310	1620	1.7	1.3	1.4	
	1825	1.4	1.8	1.6	
	2065	1.8	1.9	1.8	
	1755	1.0	1.7	1.6	
	1880	1.6	1.4	1.6	
(10) 928	635	1.0	0.5	0.8	0.7
	715	0.7	0.9	0.6	1.0
	625	0.9	0.9	0.5	0.6
	675	0.8	0.9	0.9	0.6
	705	0.8	0.7	0.8	0.8

TABLE 7.6

Volatile Burning Times (Silkstone)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	43580	13	11	13
	39280	12	10	11
	40150	10	10	12
	39100	12	10	14
	39600	9	15	12
(3) 3000	25380	8	8	8
	24930	8.5	9.5	8.5
	25170	7.5	9	7.5
	24430	9	8	7.5
	25430	8.5	6	9
(6) 1870	7060	2.7	4.4	4.5
	6130	3.1	2.9	3.2
	5640	3.1	3.6	3.4
	5940	3.6	2.8	3.3
	4720	3.8	4.2	3.8
(9) 1100	1170	1.2	1.0	0.7
	1100	1.1	1.2	1.2
	1030	0.8	1.3	1.2
	1020	0.9	1.3	1.0
	1090	0.9	1.0	0.8
(11) 776	350	-	0.25	0.3
	330	0.4	0.2	0.3
	325	0.3	0.5	0.45
	330	0.6	0.3	0.1
	350	0.3	0.4	0.3

TABLE 7.7

Volatile Burning Times (Winter)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	49820	-	12	-
	48170	13.5	-	-
	53450	11.5	-	-
	49280	-	10.5	-
(3) 3000	25200	7.5	-	7
	23400	8.5	7.5	5
	24400	7	7	8
	23950	7	8	8
	27400	8	-	8
(6) 1870	6500	2.8	3.0	2.5
	5120	2.5	2.3	2.6
	5830	2.8	2.7	2.8
	5410	2.8	2.3	2.7
	4210	2.8	-	2.8
(9) 1100	1040	1.0	0.75	0.45
	870	0.75	0.7	0.65
	1090	0.8	0.8	0.9
	1180	1.0	0.8	1.2
	1150	0.9	1.1	0.6
(11) 776	360	0.2	0.3	0.3
	290	0.4	0.25	0.2
	400	0.3	0.3	0.35
	420	0.4	0.5	0.4
	320	0.5	0.3	0.2

TABLE 7.8

Volatile Burning Times (Cowpen)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)		
		1	2	3
(1)	62880	18	14	-
4060	50830	-	-	12.5
	52720	14	-	13
	63370	12	11	12.5
	53720	10	13	12
(3)	23900	5	11	8
3000	24980	8	7	7
	23250	-	6	8
	24950	7	6	6
	26800	6	5	9
(6)	5080	3.0	1.9	2.5
1870	5370	2.8	1.6	3.0
	6430	2.8	2.6	3.0
	5640	2.6	2.0	1.2
	5750	2.1	3.2	2.8
(9)	1130	-	1.0	0.9
1100	990	0.7	0.9	0.8
	1000	0.9	0.6	0.8
	1130	-	0.6	0.9
	1070	1.4	0.8	-
(11)	390	0.4	0.3	0.5
776	410	0.4	0.5	0.5
	385	0.4	0.4	0.5
	395	0.6	0.2	0.4
	395	0.5	0.3	-

TABLE 7.9

Volatile Burning Times (High Hazel)

Fraction no.	1	2	3	4	5	6
Size: microns	4060	3270	3000	2610	2240	1870
Weight microgm.	65040	27540	26920	15720	10000	5300
Burning Times: (sec.)	14 12.8 11 11.2 13.6	11 9.6 9.4 7 11.6	8 7.5 6 8 8.8 7.6	4.9 6.4 7.1 6.8 6.2	4.5 4 4 4.9 3.8	2.08 2.68 3.16 2.8 2.4
Fraction no.	7	8	9	10	11	12
Size: microns	1550	1310	1100	928	776	649
Weight: microgm.	2940	1480	1130	540	390	223
Burning Times: (sec.)	1.88 2.2 1.6 1.76 1.28	1.24 1.2 0.84 1.0 0.96	1.0 0.8 0.88 0.6 0.92 0.8 0.68 0.68	0.42 0.4 0.38	0.24 0.36 0.32 0.44	0.24

TABLE 7.10

Volatile Burning Times (Lorraine)

Fraction no. and size: microns	Weight: microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	78440	16	17	-	19
	79500	17	-	15	-
	78700	17	-	15	15.5
	84960	18	17	15	-
(3) 3000	23960	8	10	8.5	8
	26200	7.5	8.5	8	9
	26120	8	8.5	8	7
	20575	7	5.5	8	7.5
(6) 1870	5740	2.6	3.5	3	3
	5760	-	3.3	2.5	3
	5760	2.9	-	2.7	3.5
	6700	3.2	3.7	3	2
(9) 1100	1060	0.9	0.9	0.7	0.8
	985	1.2	0.8	0.6	0.8
	1015	0.6	0.7	0.6	0.8
	1005	-	0.6	0.8	0.9
(11) 776	375	-	0.28	0.26	-
	370	0.2	0.24	-	0.3
	455	0.42	-	0.3	-
(14) 461	73.3	0.2	-	-	-

Although no theory exists at present to predict a relation between burning time and diameter, there are two alternative arguments that can be set out to suggest that a square law relationship may be expected as expressed by equation (1).

(i) Let us suppose that the coal particle is in effect a container for a volatile fluid, then we can treat the system as being equivalent to a fluid drop of low density that will lose fluid by evaporation from its surface. The square law of equation (1) then follows, since the burning drop has also been shown to obey such a square law (see Fig.1.). The difficulty of this application however is that it supposes that evaporation takes place quite uniformly and gently from a liquid surface, whereas in fact the evolution was observed to be vigorous and was generally channelled by the solid matrix into irregular flaming jets that issued with some force; furthermore, the diameter of the holding matrix did not alter overmuch during the volatile expulsion, and then it increased because of swelling, instead of decreasing as a liquid drop would do.

(ii) An alternative theory that can be set up to dispose of these difficulties can possibly be based on the observation (62) that volatile emission seems to decay with time roughly according to the relaxation exponential law (save only for the more firmly bound hydrogen - see sec. 3). If we assume that the rate of escape of the potentially fluid material is proportional to the area of a "surface of escape", the variable in this surface area is the nominal area of the particle, which is proportional to its diameter squared. If we also assume that the combustion ceases when the rate of volatile emission drops below a certain critical value, it then follows that the burning times should be finite and proportional to the square of the diameter.

In view of the somewhat arbitrary nature of the definition of diameter, it was thought preferable to check any theoretical relationships on a weight basis, since this was thought to have been more accurately determined than was diameter; there was also the consideration that, since only a fraction of the coal material was involved, the initial weight was more easily converted into the real parameter - actual weight burned - but this was not true of diameter. If a square law relation with diameter is to be expected, the variation with weight obtained by combining equations (1) and (2) should be a fractional power function of the form

$$t_v = K'_v.(w_o)^{n'_v}$$

Where K'_v and n'_v are the constants to be determined; and for a sphere n'_v should have a value of 2/3 or 0.667.

The validity of the above empirical equation is illustrated by the appropriate plots (Figs. 7.1 to 7.10); and the values of the constants are given in Table 8a. As this shows, the values of n'_v are approximately correct, thus indicating that an approximate square law relationship does exist. To check this on the diameter basis as defined, these constants have been recalculated by substitution for weight using equation (2). The new values of K_v and n_v (diameter basis) are listed in Table 8b which shows that the results do obey an approximate square law relationship. The values of K_v are also seen to be in the order of magnitude found for the liquid drops (see Table 1), in accordance with hypothesis (i) above.

Although these data provide support for treating the system as being equivalent to an oil drop, the physical system is still an emission process that is likely to be determined by the temperature alone. In a flame therefore the burning time should remain a square law function of diameter, and be independent of oxygen concentration, provided only that there is sufficient oxygen for combustion.

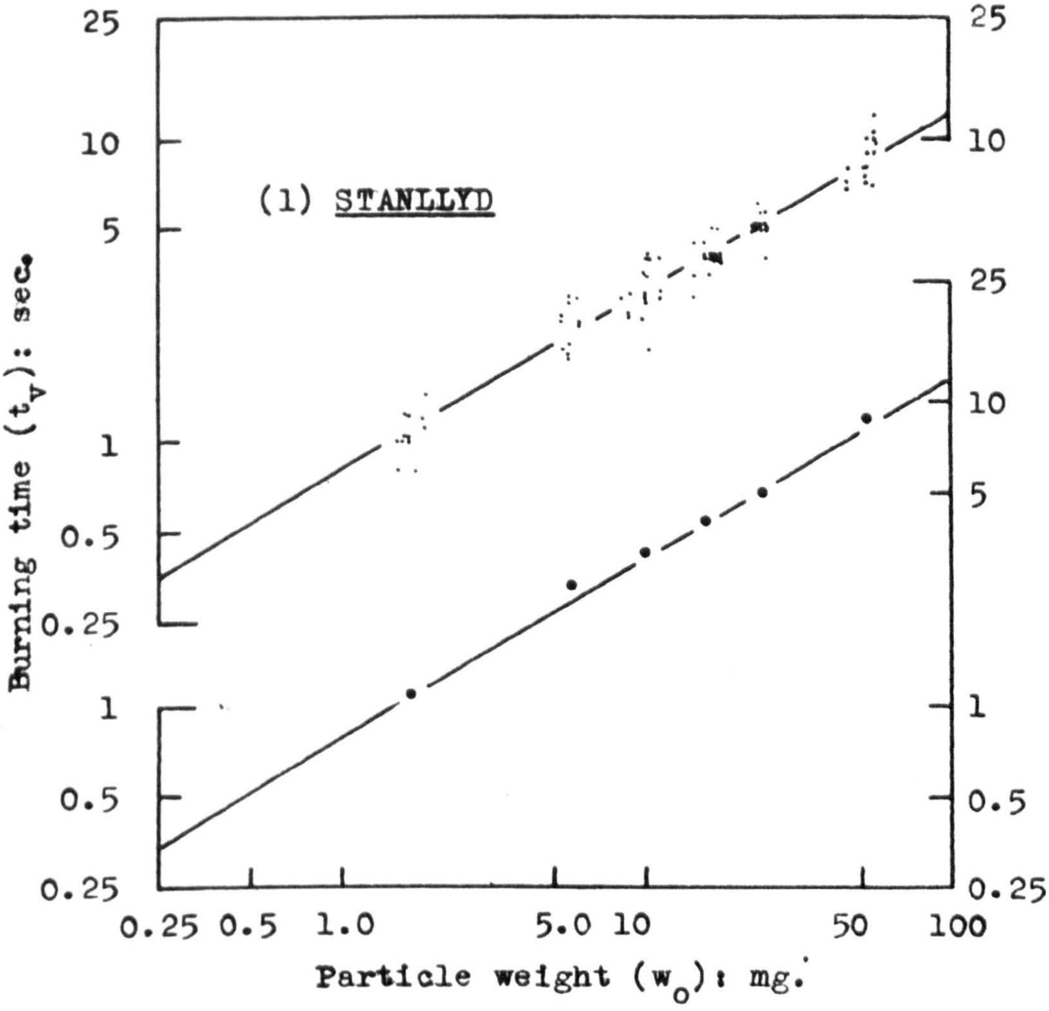


Fig. 7.1 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (82 points)
(Bottom) Averaged plot.

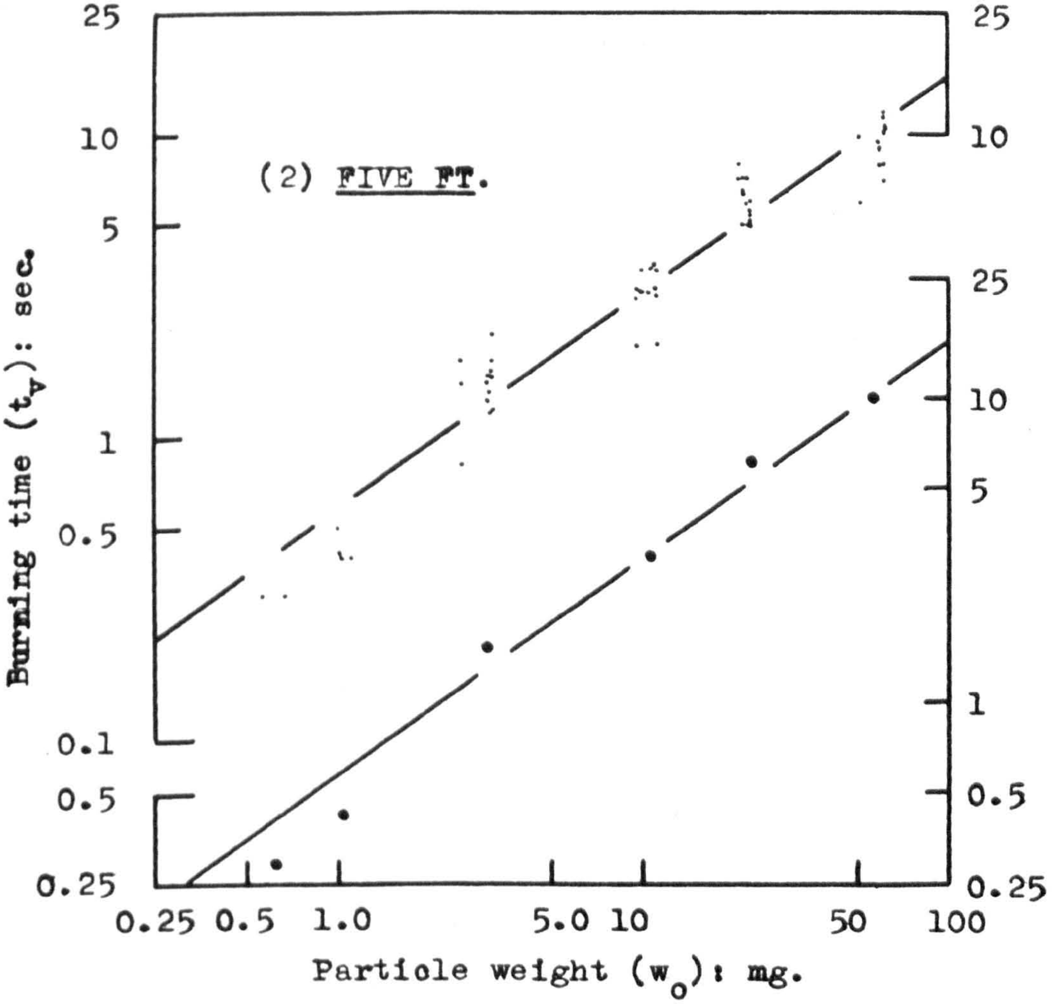


Fig. 7.2 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (62 points)
(Bottom) Averaged plot.

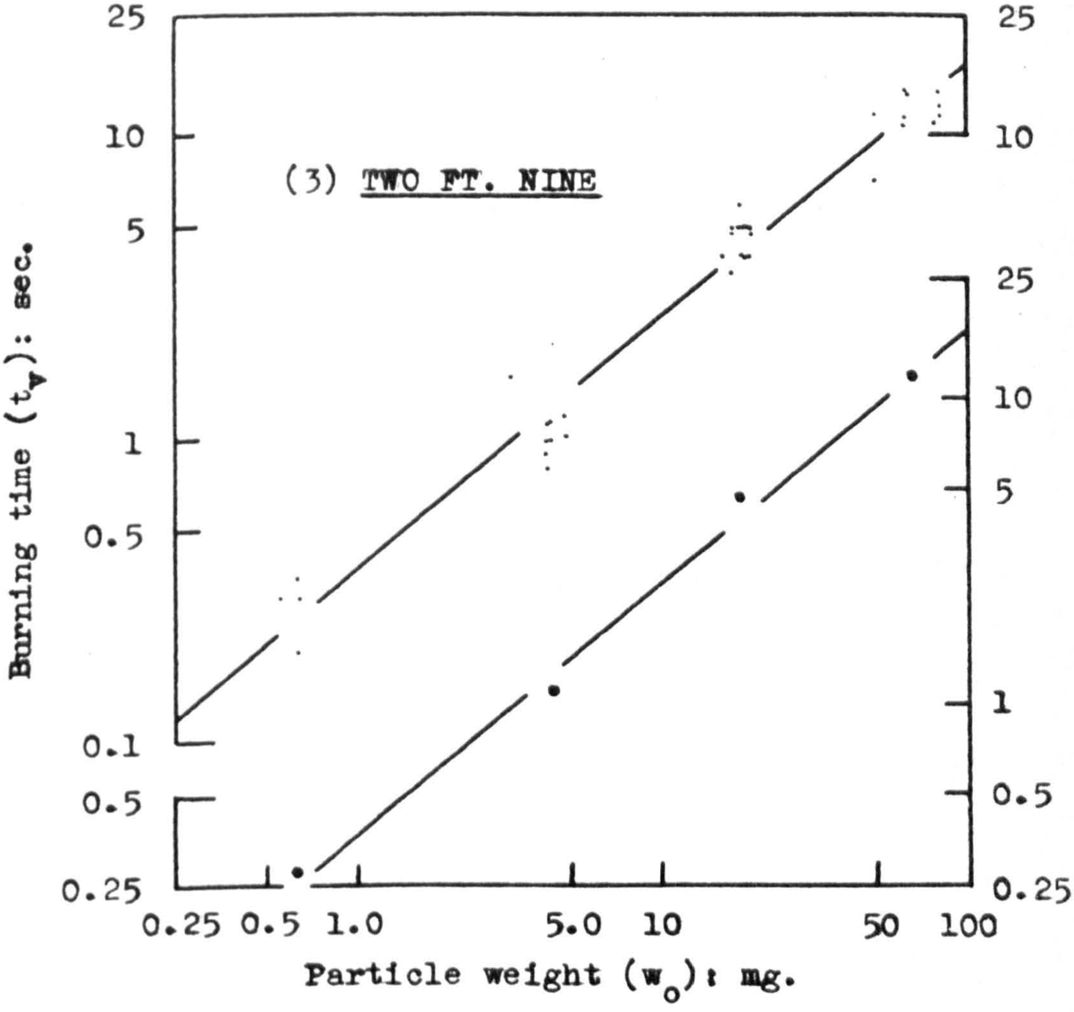


Fig. 7.3 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (37 points)

(Bottom) Averaged plot.

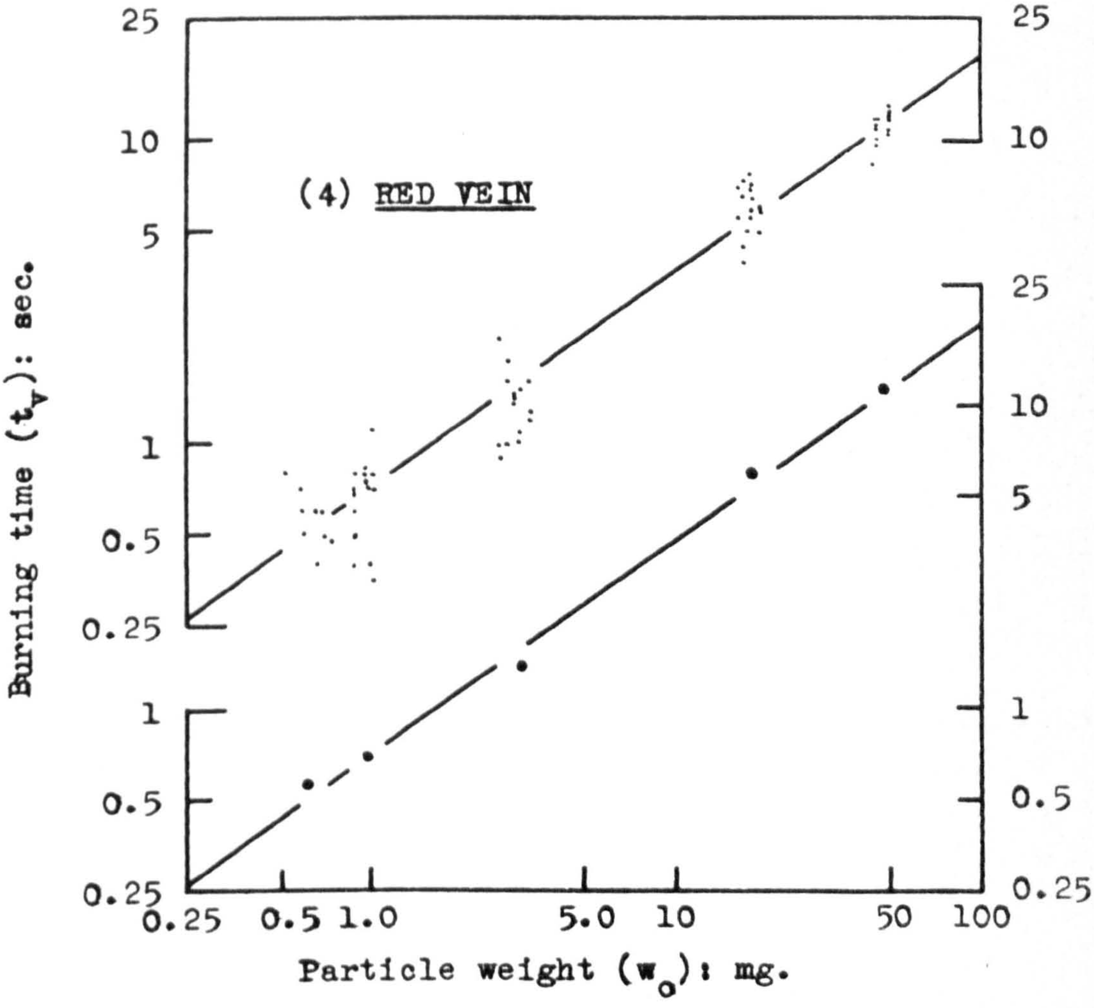


Fig. 7.4 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (64 points)
(Bottom) Averaged plot.

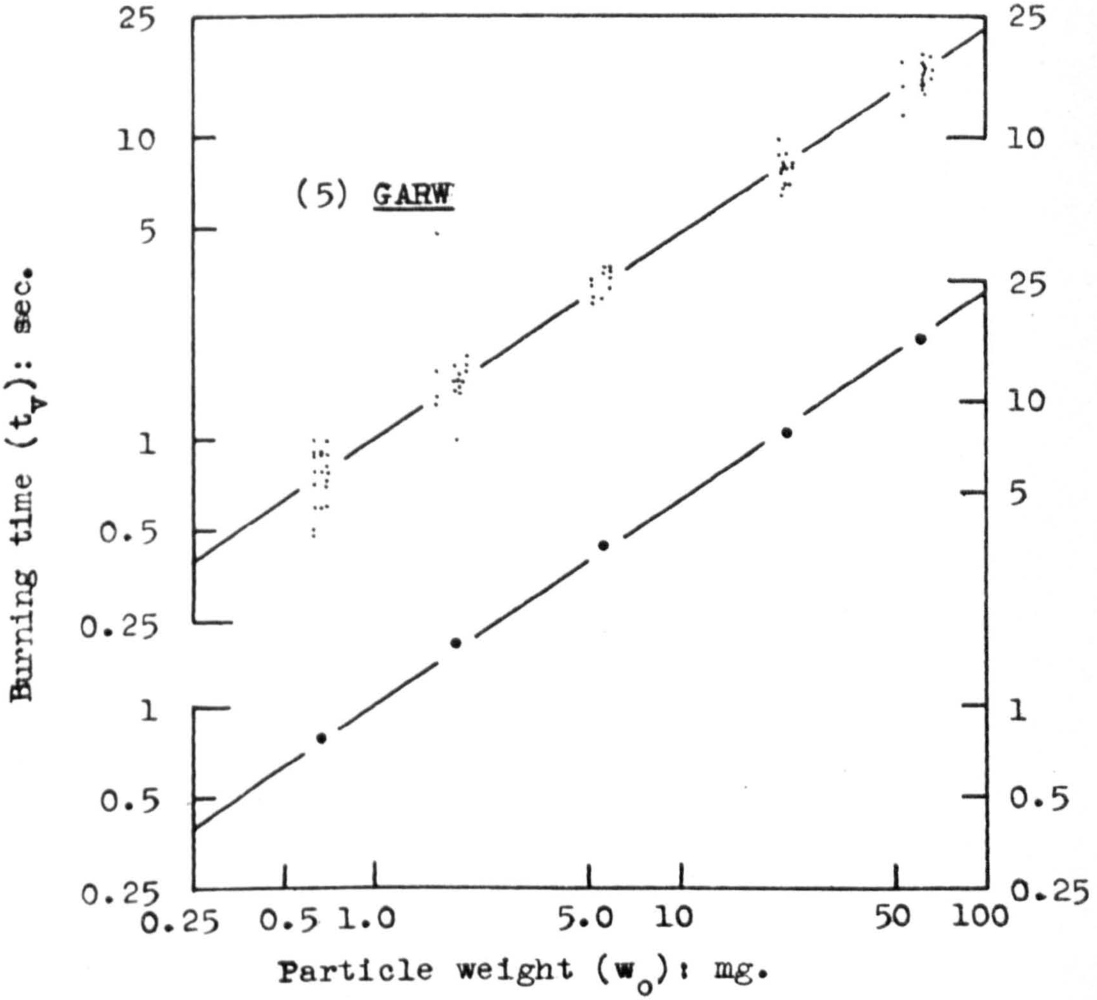


Fig. 7.5 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (80 points)
(Bottom) Averaged plot.

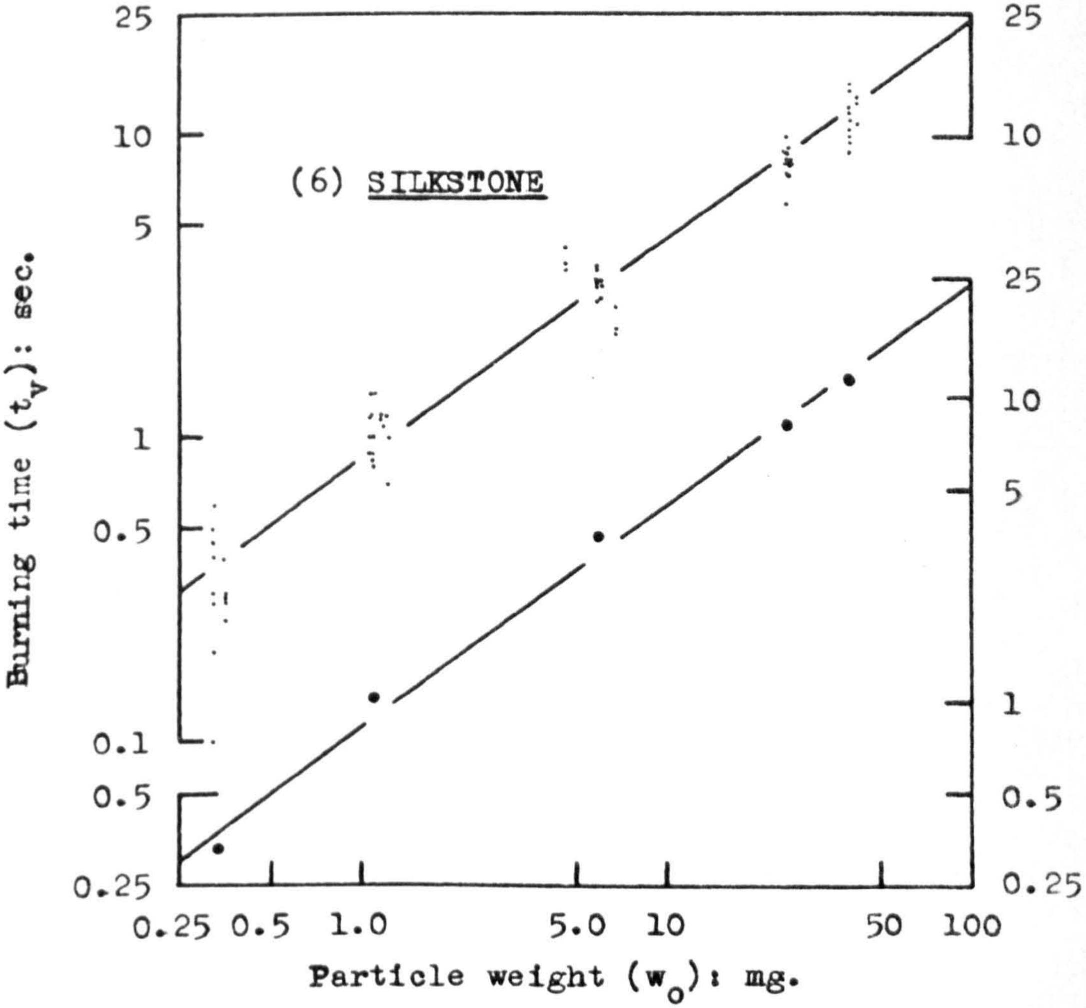


Fig. 7.6 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (74 points)
(Bottom) Averaged plot.

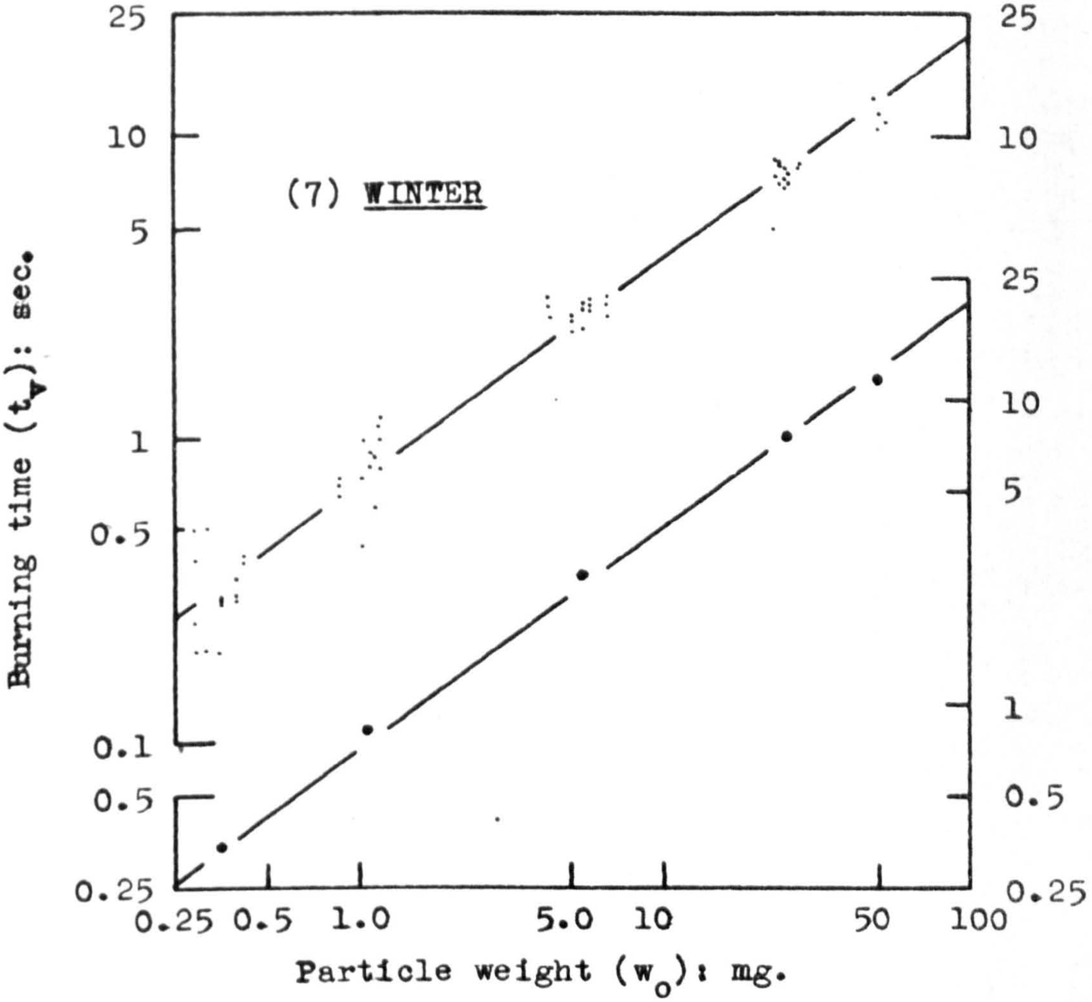


Fig. 7.7 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (61 points)
(Bottom) Averaged plot.

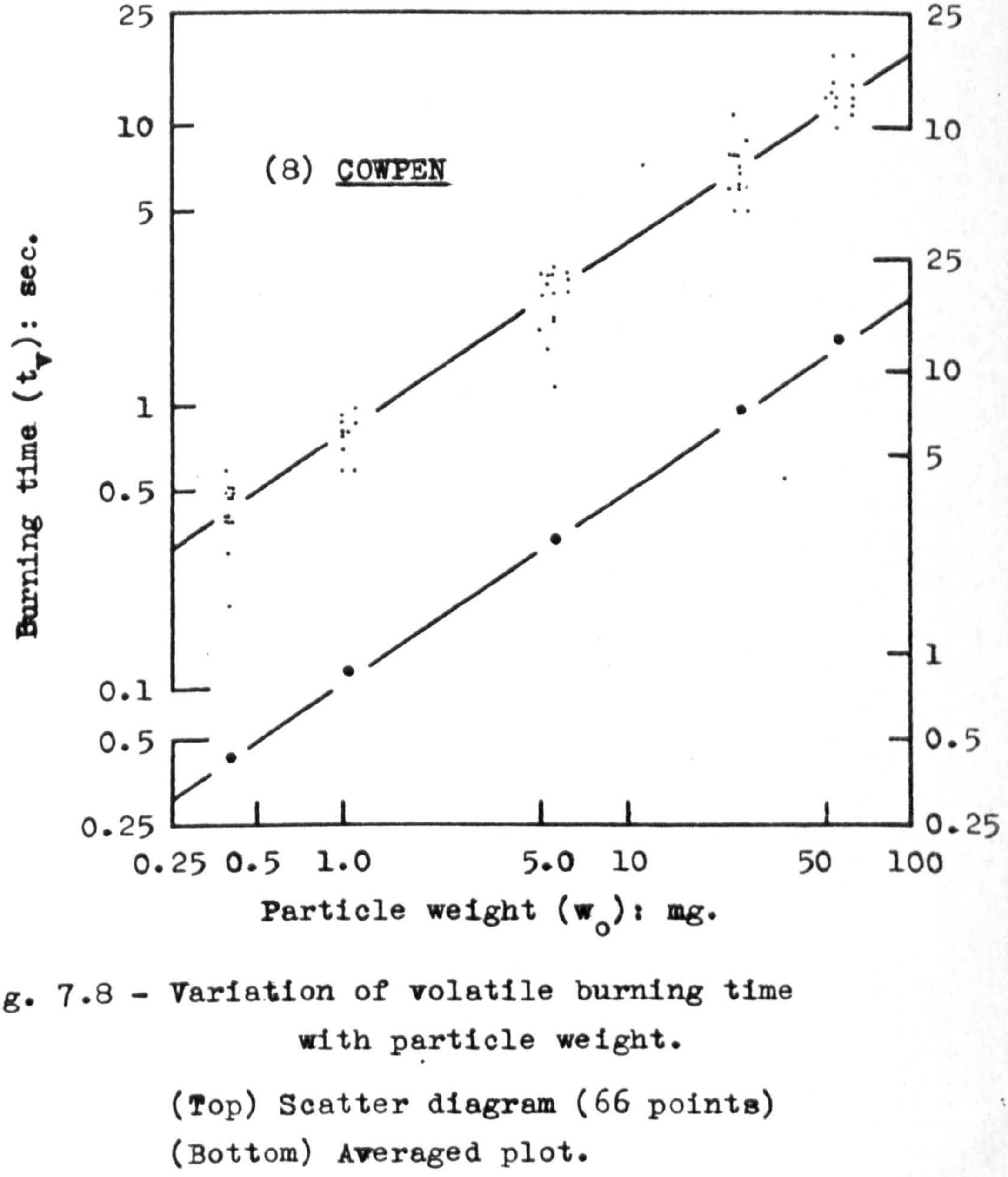


Fig. 7.8 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (66 points)

(Bottom) Averaged plot.

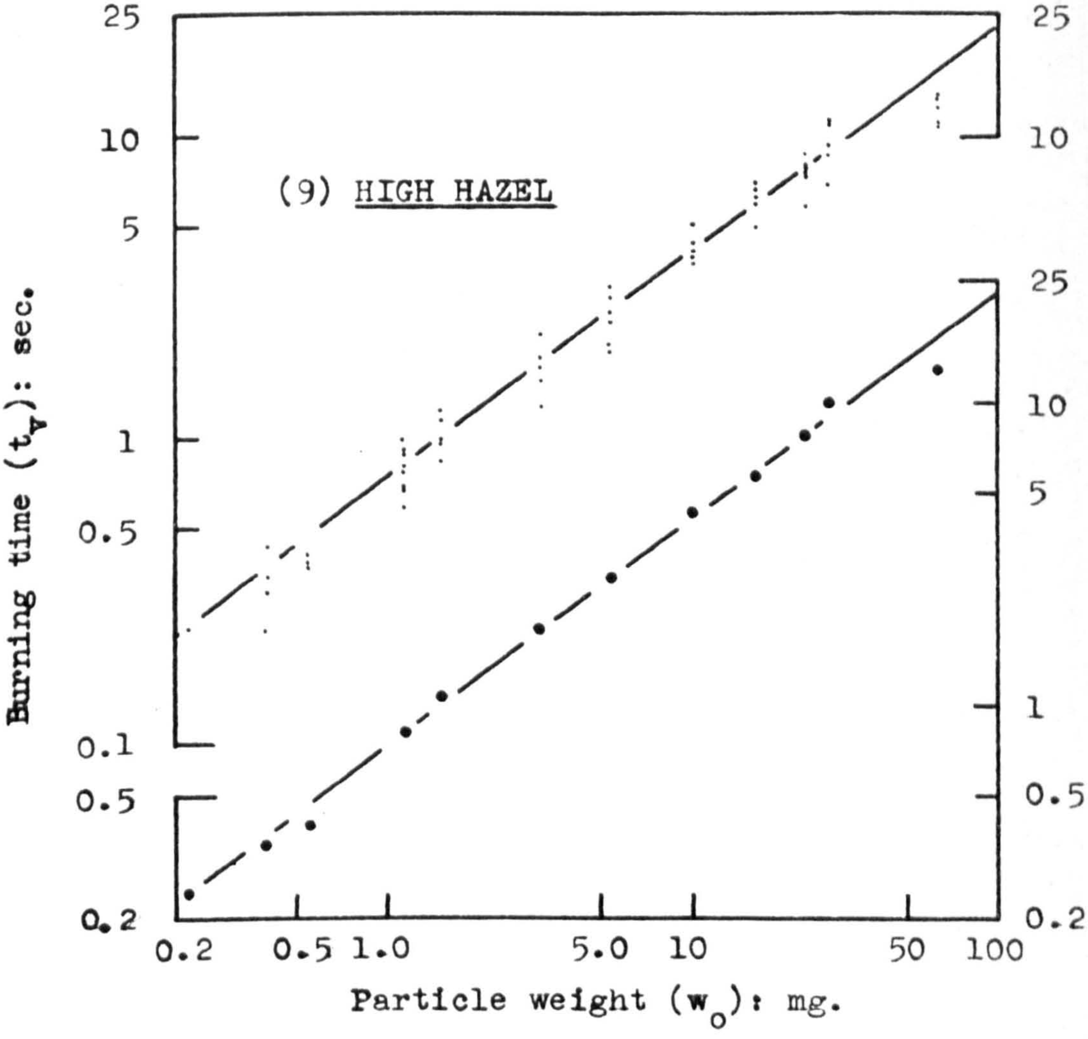


Fig. 7.9 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (57 points)
(Bottom) Averaged plot.

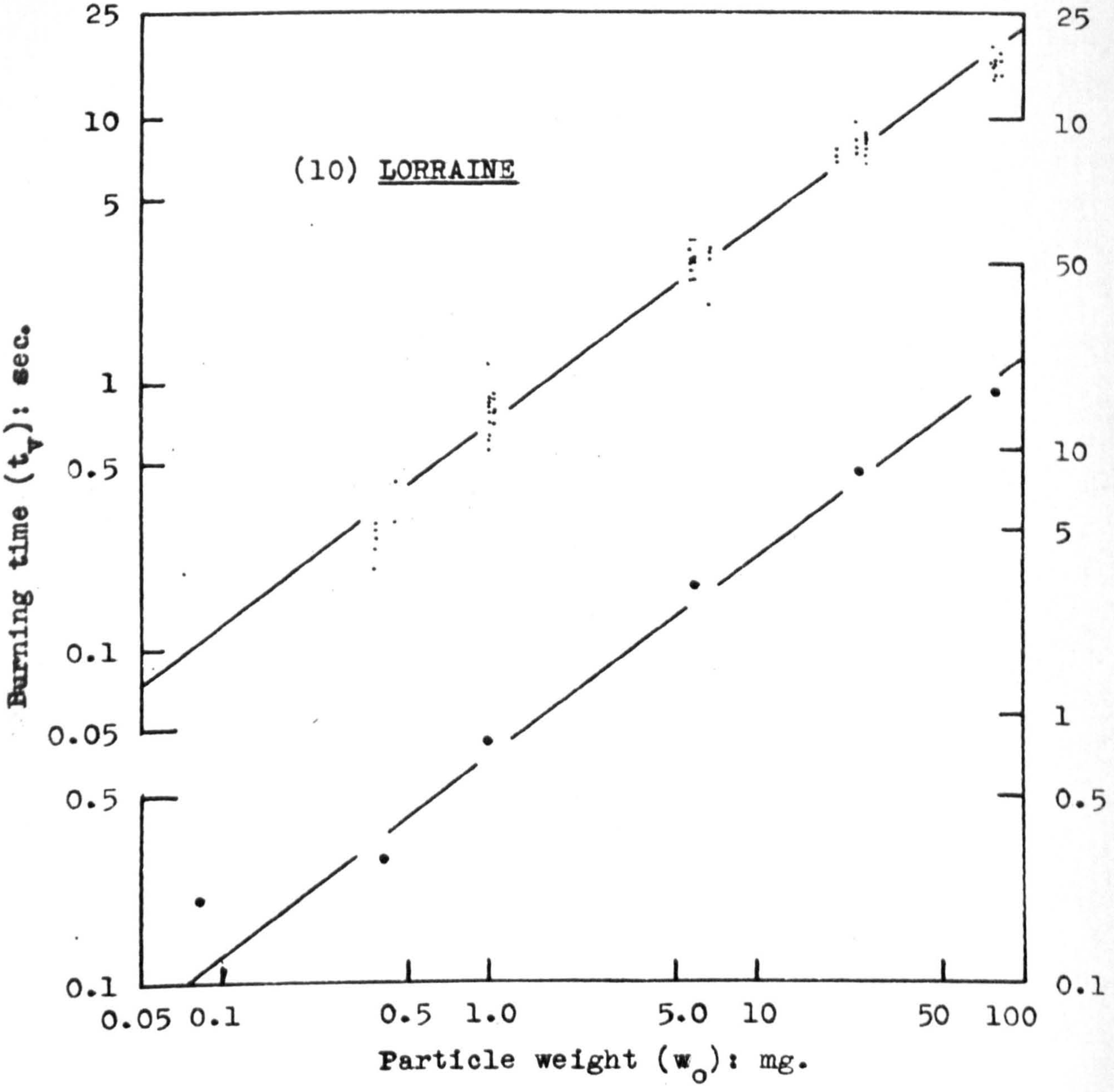


Fig. 7.10 - Variation of volatile burning time with particle weight.

(Top) Scatter diagram (65 points)
(Bottom) Averaged plot.

TABLE 8.a

Experimental Values of Burning Constants for Volatile Combustion

(Weight basis: c.g.s. units)

	Coal	%C (d.m.f.)	n_v'	K_v'
1	Stanllyd	93.0	0.594	48.4
2	Five ft.	91.8	0.724	80.7
3	Two ft. Nine	91.2	0.836	107
4	Red Vein	89.7	0.725	102
5	Garw	88.9	0.676	102
6	Silkstone	86.9	0.728	120
7	Winter	84.0	0.732	106
8	Cowpen	82.7	0.678	91.4
9	High Hazel	81.9	0.750	140
10	Lorraine	79.3	0.733	104

TABLE 8.b

Experimental Values of Burning Constants for Volatile Combustion

(Diameter basis: c.g.s. units)

	Coal	%C (d.m.f.)	n_v	K_v
1	Stanllyd	93.0	1.82	44.6
2	Five ft.	91.8	2.32	80.0
3	Two ft. Nine	91.2	2.63	120
4	Red Vein	89.7	2.19	86.6
5	Garw	88.9	2.06	96.8
6	Silkstone	86.9	2.19	91.6
7	Winter	84.0	2.24	93.6
8	Cowpen	82.7	2.15	91.4
9	High Hazel	81.9	2.28	134
10	Lorraine	79.3	2.14	98.9

6.3 The Residue Combustion - The values of burning time obtained are listed in Tables 9.1 to 9.10. During combustion, and noticably near the end of the volatile emission, a number of the particles decrepitated or exploded, so some results were lost on this account. This happened mainly to the largest particles; also with the larger particles, some fell off during the residue combustion, generally because the reaction had eaten under the cement holding the particle to the silica fibre. When a particle fell off, it did so complete except in the case of the anthracite; with this last, the bonding that the other particles experienced during coking did not occur, and in a number of instances with this coal the particle sheared in two under its own weight, leaving one half of the particle still attached to the silica fibre. For these and similar reasons, records were not obtained from all the particles mounted. Of 1300 particles mounted, just over 900 values of burning time were obtained.

Again the theoretical relationships were checked on a time/weight basis (see Figs. 8.1 to 8.10) for substantially the same reasons as those given in the previous section (sec. 6.2). The values of the constants (K_r' and n_r') obtained on this weight basis are listed in Table 10a,

TABLE 9.1

Residue Burning Times (Stanllyd)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3			1	2	3	4
(1) 4060	55980	-	258	310	(8) 1310	1540	-	26	28	
	45830	-	210	-		1870	28.5	44	43	
(3) 3000	23150	164	-	-		1660	47	33	34	
	23770	160	-	217		1610	41.5	36	33	
	24000	-	188	-		1720	36	32	-	
(4) 2610	16550	-	-	145	(10) 928	625	-	-	27	13
	17770	150	-	-		660	10	-	15	-
	16680	160	-	167.5		640	19	31.5	-	-
	14420	145	-	-		585	-	22	20	17
	16080	-	135	-		620	-	11	10	18
(5) 2240	9940	120	110	-	(11) 776	325	-	8	8.5	17
	8790	112.5	107.5	117.5		325	18	17	7	-
	11220	110	112.5	125		360	16	17.5	15	-
	10260	112.5	125	102.5		365	12.5	-	15	16
	9990	102.5	-	-		335	-	11	-	14
(6) 1870	5810	94	80	72	(12) 649	190	-	9	4.8	-
	5250	79	60	73		163.3	-	-	8.8	9.8
	6020	65	69	75		173.3	8.4	4.8	10.8	-
	6640	120	-	-		173.3	-	-	-	3.8
	6150	76	89	-		183.3	-	-	-	6.8

TABLE 9.2

Residue Burning Times (Five ft.)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)		
		1	2	3
(1) 4060	58550	280	-	257
	60430	-	201	-
(3) 3000	22380	-	126	112.5
	22130	-	128	131
	20900	-	115	89
	21550	87	-	116.5
(5) 2240	11320	70	71	80
	11120	-	-	72
	10590	64	-	-
	9590	-	47	60.5
(7) 1550	3060	34.8	-	51.8
	3240	34	29.5	40.2
	2540	26	30	49.4
	3240	37.2	41	-
	3200	-	35.5	30.6
(9) 1100	980	18.4	16.9	14.8
	1035	-	19.4	-
	1095	19.2	22.5	-
	1025	19.5	14.2	17.8
	1030	16.2	-	22.2

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)				
		1	2	3	4	5
(10) 928	650	18	15.8	14	11	12
	685	16.6	12.8	11.2	10.8	13.4
	625	-	14.4	12.2	11.6	-
	700	12.4	11.6	13.8	14.2	14
	565	11	16.7	-	12	-
(12) 649	160	5.2	5.2	5.2	4.4	-
	173.3	3.2	7.2	5.4	7.8	-
	186.7	5.6	-	5.4	6.8	-
	190	-	6.6	6.6	4.8	-
	180	6	6	4.5	3.3	-
(14) 461	56.67	3.7	3.5	3	3.4	3.4
	60	3	4.5	3.6	3.6	3
	53.33	4	2.8	3.2	5.4	-
	70	5.6	3.1	2.9	5.2	-
	70	3.6	3.6	2.1	1.6	-
(16) 324	17.5	2.6	1.6	-	-	-
	15	1.5	-	-	1.3	-
	15	1.4	-	-	1.7	-
	17.5	1.2	-	1.5	-	-
	20	1.2	-	-	-	-

TABLE 9.3

Residue Burning Times (Two ft. Nine)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	64880	-	-	247	
	49280	-	-	175	
	63200	-	255	194	
	82730	-	-	167	
	76770	-	-	163	
(4) 2610	18470	90	-	-	
	19400	69	102	-	
	17020	64.5	70	92.5	
	19630	104	-	102	
	15550	66	90	87	
(7) 1550	4670	20	-	-	
	4200	23.5	19	-	
	3270	-	23.5	-	
	4820	-	23.6	20.2	
(10) 928	656.3	-	7.8	7.0	
	693.8	-	4.1	-	
	625.0	8.2	9.7	7.2	
	562.5	-	7.7	5.2	
	637.5	11.2	-	5.8	
(13) 550	137.5	2.32	-	2.8	-
	125	2.04	1.36	-	-
	145.7	1.32	1.92	-	2.42
	137.5	-	5.68	1.32	-
	108.3	1.80	2.76	2.24	2.08
(16) 324	22.5	-	-	1.68	0.4
	22.5	0.76	0.36	0.72	0.96
	30	0.4	-	0.76	0.92
	22.5	-	-	1.0	-

TABLE 9.4

Residue Burning Times (Red Vein)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3			1	2	3	4
(1)	46270	198	203	202	(10)	590	10.6	10.6	-	
4060	46400	-	-	251	928	590	8.4	12.3	8.4	
	49700	248	248	166		710	11.6	-	-	
	45530	177	-	185		670	6.6	8.4	8.4	
	50450	-	178	-		525	6.8	7.4	12.8	
(4)	16000	98	-	92	(13)	93.33	5	1.32	4.52	-
2610	17600	113	-	99	550	96.67	1.44	-	2.8	3.28
	17920	96	99	162		113.33	-	-	2.56	3.12
	19350	107	-	125		123.33	2.6	3.76	3.24	-
	16650	80	78	115		120.00	-	3	1.52	2.88
(7)	3100	32.4	27.2	26.8	(15)	50	-	-	1.0	-
1550	2660	-	-	13.5	388	52.5	-	-	1.32	1.88
	3130	20.3	16.6	29.4		40	1.0	-	-	-
	3350	37.7	19.2	44		42.5	1.32	1.28	-	-
	3040	20	13.7	31.6		45	1.25	-	-	1.2
(9)	900	8.2	14.0	10.6	(16)	10	-	-	0.68	-
1100	900	10.6	12.6	9.0	324	30	-	-	-	1.36
	1005	9.4	15.4	16.6		12.5	-	1.2	1.4	-
	1045	9.8	14.5	7.2						
	960	10.2	8.9	19.2						

TABLE 9.5

Residue Burning Times (Garw)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	64520	232	278	-	
	67230	-	225	277	
	52880	315	230	184	
	60980	280	270	200	
	61670	250	232	225	
(3) 3000	21130	134	113	135	
	23520	117.5	135	107	
	21830	100	161	127	
	22750	-	157	121	
	21550	115	129	142	
(6) 1870	6150	55.6	48.6	43	
	6020	72	49	72	
	5180	42.6	37.6	55.6	
	5180	78	44.2	67	
	5560	47.2	43.4	55	
(8) 1310	1620	21.5	16.8	22.2	
	1825	32	18.6	21.4	
	2065	22.4	21.8	30.3	
	1755	16.2	29.6	26.4	
	1880	23.2	19.6	24.6	
(10) 928	635	10	9.5	10.6	8.3
	715	11.5	14.3	11	23.6
	625	7.8	14.6	8.5	14.6
	675	12.8	11.4	10.3	12
	705	9	8.8	12.8	10.6
(13) 550	103.3	7	5.1	4.8	2
	116.7	-	3.8	4.4	5.4
	100	7.7	2.5	-	2.6
	130	7	-	4.4	2.7
	103.3	2	2.2	3	-
(16) 324	32.5	-	1.1	0.8	1.6
	30	2.1	1.8	2.1	2.6
	32.5	1.1	2	1.8	1.5
	30	1.4	1.8	2.4	2.2
	27.5	-	-	1.2	1.0

TABLE 9.6

Residue Burning Times (Silkstone)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1)	43580	152	140	141	
4060	39280	126	114	111	
	40150	134	127	145	
	39100	129	119	142	
	39600	101	157	128	
(3)	25380	90	83.5	85	
3000	24930	108	115	83.5	
	25170	90	102	92	
	24430	91	86	89	
	25430	102	63	-	
(6)	7060	25.4	56.6	46.6	
1870	6130	36.4	32.2	43.2	
	5640	39.2	32.8	35.6	
	5940	38.8	29.2	33.4	
	4720	32.6	46.5	36.0	
(9)	1170	14.8	10.8	9.2	
1100	1100	10.4	13.1	9.2	
	1030	11.2	15.0	10.8	
	1020	7.0	16.0	9.5	
	1090	11.3	13.2	13.2	
(11)	350	-	4.1	-	-
776	330	4.8	3.8	-	-
	325	3.8	-	4.5	5.7
	330	6.4	4.2	2.1	-
	350	4.6	4.4	6.0	3.8
(14)	63.33	-	0.88	1.56	-
461	73.33	0.80	0.96	0.80	-
	66.67	1.28	-	0.80	0.80
	86.67	0.92	1.24	1.16	1.64
	83.33	1.36	1.56	1.28	0.40
(16)	27.5	-	-	0.48	0.72
324	37.5	0.64	0.84	0.80	-
	25.0	-	0.76	0.52	-
	20.0	0.84	0.48	0.60	0.64
	27.5	0.32	0.44	0.52	-

TABLE 9.7

Residue Burning Times (Winter)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	49820	-	148	-	
	48170	155	-	-	
	53450	152	-	-	
	49280	-	148	-	
(3) 3000	25200	89	-	92.5	
	23400	97	96	73.5	
	24400	90	95	101	
	23950	88	89	90	
	27400	105	-	102	
(6) 1870	6500	41.6	43.6	30.8	
	5120	32	32	33.4	
	5830	32	37.8	34	
	5410	35.2	31.2	34.6	
	4210	33.5	-	35	
(9) 1100	1040	12.4	13.8	7.8	
	870	10.4	9.8	8.7	
	1090	9.2	10.0	16.5	
	1180	10.8	12.2	16.0	
	1150	11.7	14.1	7.8	
(11) 776	360	5.8	4.6	3.7	5.0
	290	5.0	4.8	4.9	3.8
	400	4.8	4.9	3.4	5.0
	420	5.8	10.6	5.6	7.0
	320	6.8	4.8	3.8	2.8
(14) 461	70	1.12	2.0	2.24	1.76
	96.67	1.56	2.04	2.12	2.2
	80	1.80	1.48	2.0	1.64
	83.33	1.08	2.8	2.48	1.56
	73.33	1.20	1.56	2.12	1.68
(16) 324	20	0.48	1.04	0.44	0.2
	22.5	0.68	0.6	-	0.56
	20	0.48	0.44	0.6	0.48
	27.5	0.76	1.4	0.8	0.6
	22.5	1.08	0.8	1.08	0.4

TABLE 9.8

Residue Burning Times (Cowpen)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1) 4060	62880	240	234	-	
	50830	-	-	190	
	52720	154	-	-	
	63370	-	-	194	
	53720	-	-	151	
(3) 3000	23900	-	113	122	
	24980	110	130	-	
	23250	-	70	100	
	24950	80	-	92	
	26800	97	83	65	
(6) 1870	5080	49	37	41.4	
	5370	53.6	24.4	58.6	
	6430	58	46.8	45.4	
	5640	26.5	35	-	
	5750	20.2	49	43.6	
(9) 1100	1130	-	17.6	13	
	990	16.4	12.6	12	
	1000	15.2	17.2	12.2	
	1130	19.4	10.8	15.6	
	1070	15	13.6	-	
(11) 776	390	7.2	7	7.2	6
	410	6.8	4.6	7	7.8
	385	6.6	7.8	5.8	10.1
	395	11.5	15.5	7.8	7.4
	395	5.6	6.4	4.7	7.6
(13) 550	106.7	2.4	4.4	4.6	2.4
	96.7	1.9	5.0	5.1	1.8
	106.7	2.2	5.0	-	2.8
	96.7	3.1	2.6	3.0	2.8
	110.0	3.8	3.9	2.4	2.6
(16) 324	20	1.6	1.3	1.2	2.4
	20	1.0	1.3	-	2.0
	20	-	1.8	-	1.3
	20	1.6	0.9	1.5	1.1
	17.5	-	0.9	1.8	-

TABLE 9.9

Residue Burning Times (High Hazel)

Fraction no.	2	3	4	5	6
Size: microns	3270	3000	2610	2240	1870
Weight: microgm.	27540	26920	15720	10000	5300
Burning Times: (sec.)	116 124.2 141.4	106 97	61.25 90 82 85 86	68 68.5 77.5	37.52 34.4 43.76 43.0 38.8

Fraction no.	7	8	9	10	11
Size: microns	1550	1310	1100	928	776
Weight: microgm.	2940	1480	1130	540	390
Burning Times: (sec.)	23.6 31.0 23.6 28.4 22.8	13.08 17.0 12.84 16.0 15.08	11.5 11.0 16.2 13.2 17.4 11.44 10.68 7.08	9.1 7.52 7.44 10.6 4.6	4.48 6.2 9.0 3.74 5.42 5.16

Fraction no.	12	13	14	15	16
Size: microns	649	550	461	388	324
Weight microgm.	223	140	70	43.3	24.3
Burning Times: (sec.)	4.44 3.2 5.94 3.84 4.0	2.75 2.0 3.8 3.8 2.4 2.64 2.9	2.73 1.5 3.36 2.2 3.2	1.8 1.88 1.6 1.7 1.46	0.8 0.3 0.6 0.77 1.03 1.5

TABLE 9.10

Residue Burning Times (Lorraine)

Fraction no. and size: microns	Weight microgm.	Burning Times (sec.)			
		1	2	3	4
(1)	78440	149	189	-	193
4060	79500	-	-	179	-
	84960	-	227	206	-
(3)	23960	-	-	86	78
3000	26200	118	102	105	65
	26120	104.5	105.5	-	-
	20575	76	-	88.5	85
(6)	5740	28.3	33.3	37.4	-
1870	5760	36.4	-	39.2	24.6
	6700	28	46.4	43	33.2
(9)	1060	11.7	9.8	7.4	10.1
1100	985	12.5	8.4	-	11.7
	1015	10.7	10.0	10.6	8.2
	1005	-	10.0	11.8	11.8
(11)	380	6.2	7.08	6.72	6.04
776	375	-	5.8	5.0	-
	370	4.8	4.36	5.36	6.58
	455	6.44	6.2	5.88	5.52
(14)	83.3	-	-	1.56	1.36
461	73.3	1.94	1.86	2.04	1.88
	86.7	2.08	1.92	2.04	2.52
	86.7	2.52	1.92	1.88	2.44
(16)	37.5	0.74	-	-	0.96
324	30.0	-	1.12	1.02	-
	27.5	-	0.92	0.76	0.92
	30.0	1.52	1.20	0.68	1.56
	30.0	0.92	0.66	0.80	0.92

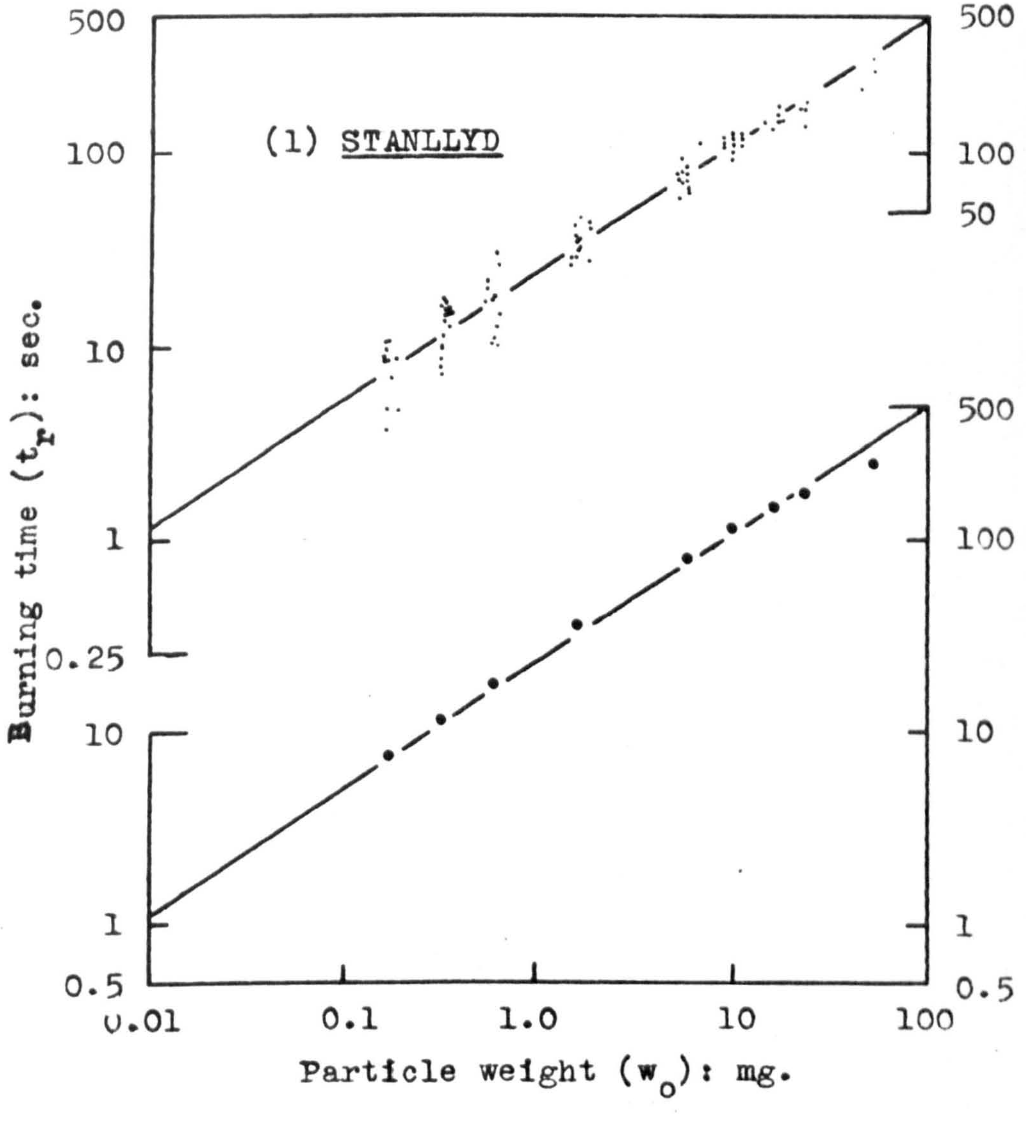


Fig. 8.1 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (90 points)
(Bottom) Averaged plot.

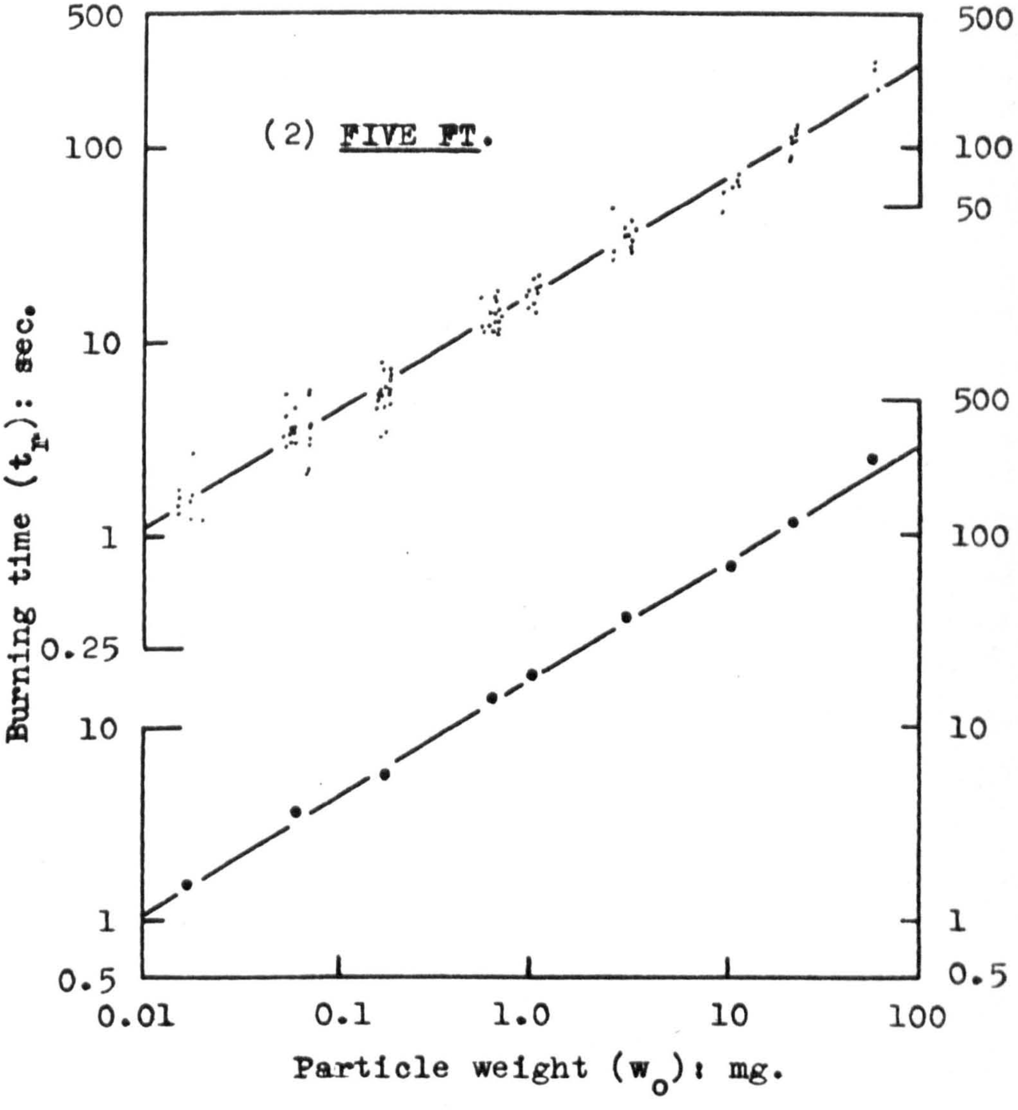


Fig. 8.2 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (111 points)
(Bottom) Averaged plot.

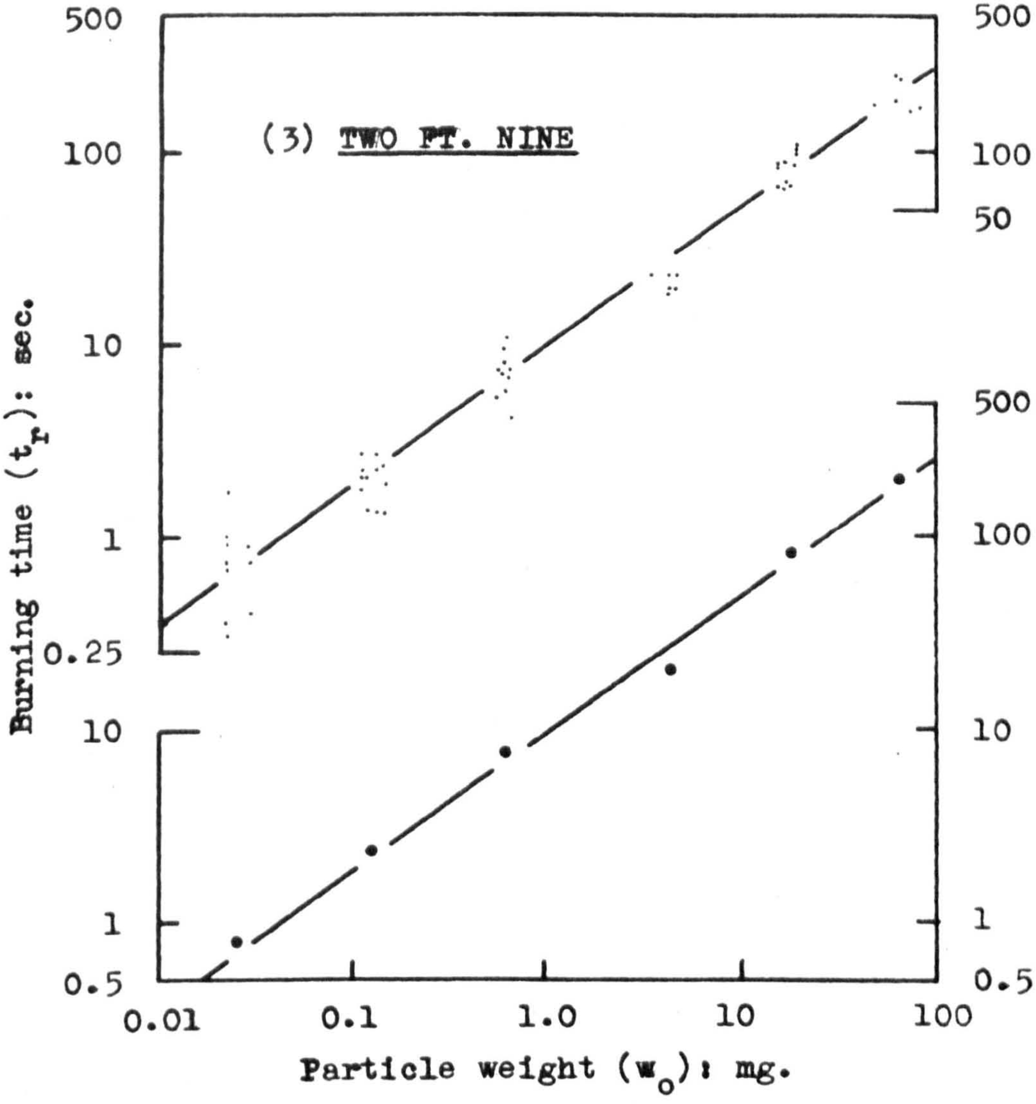


Fig. 8.3 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (56 points)

(Bottom) Averaged plot.

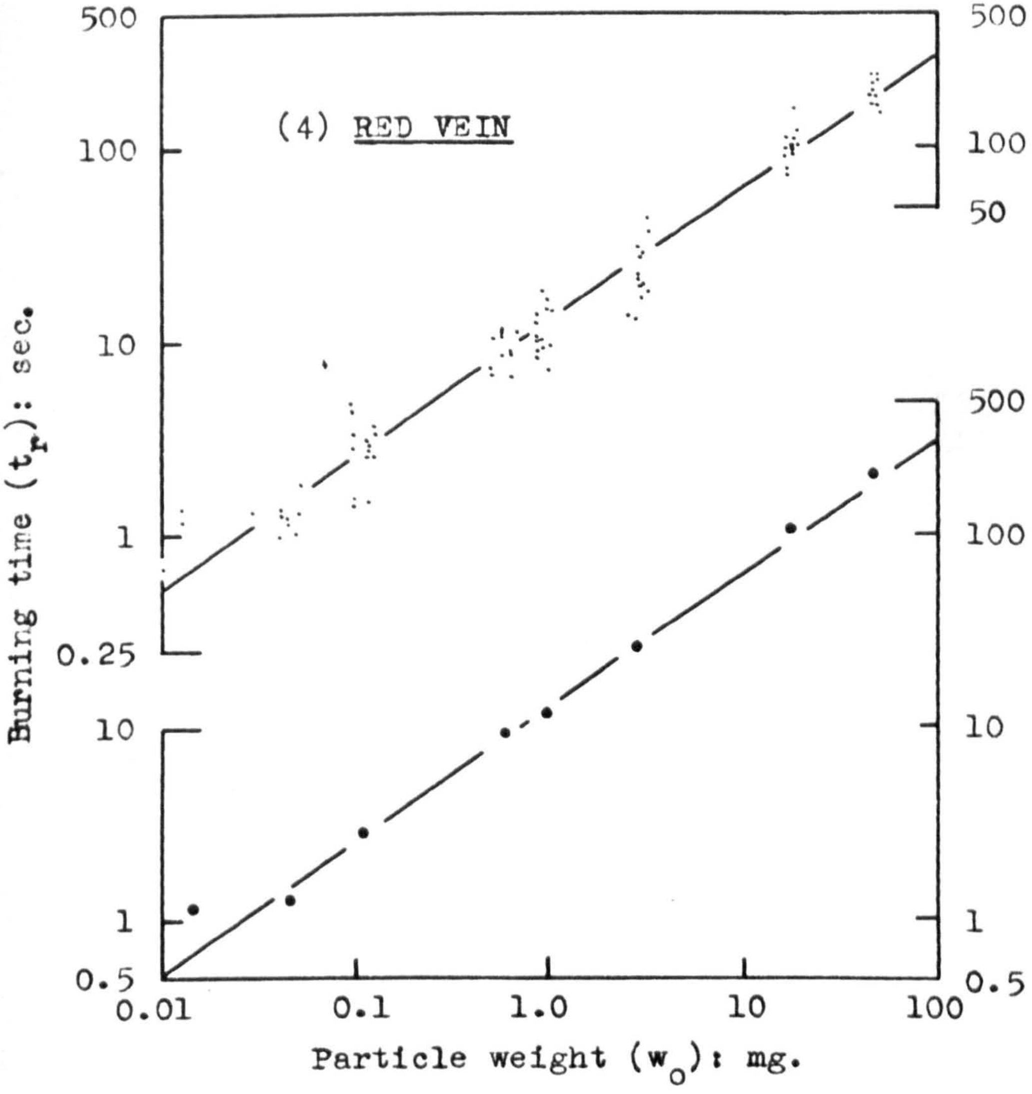


Fig. 8.4 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (88 points)
(Bottom) Averaged plot.

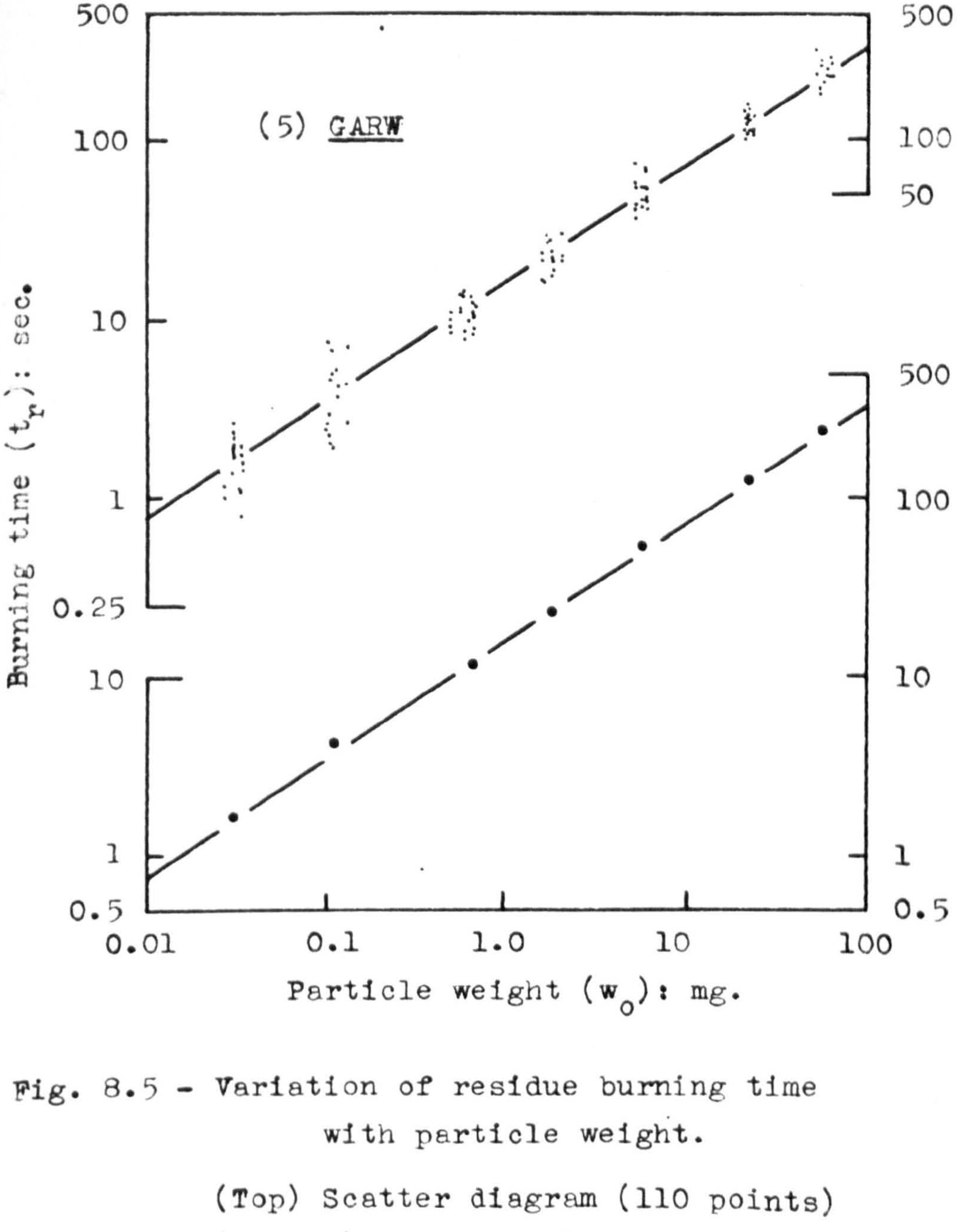


Fig. 8.5 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (110 points)
(Bottom) Averaged plot.

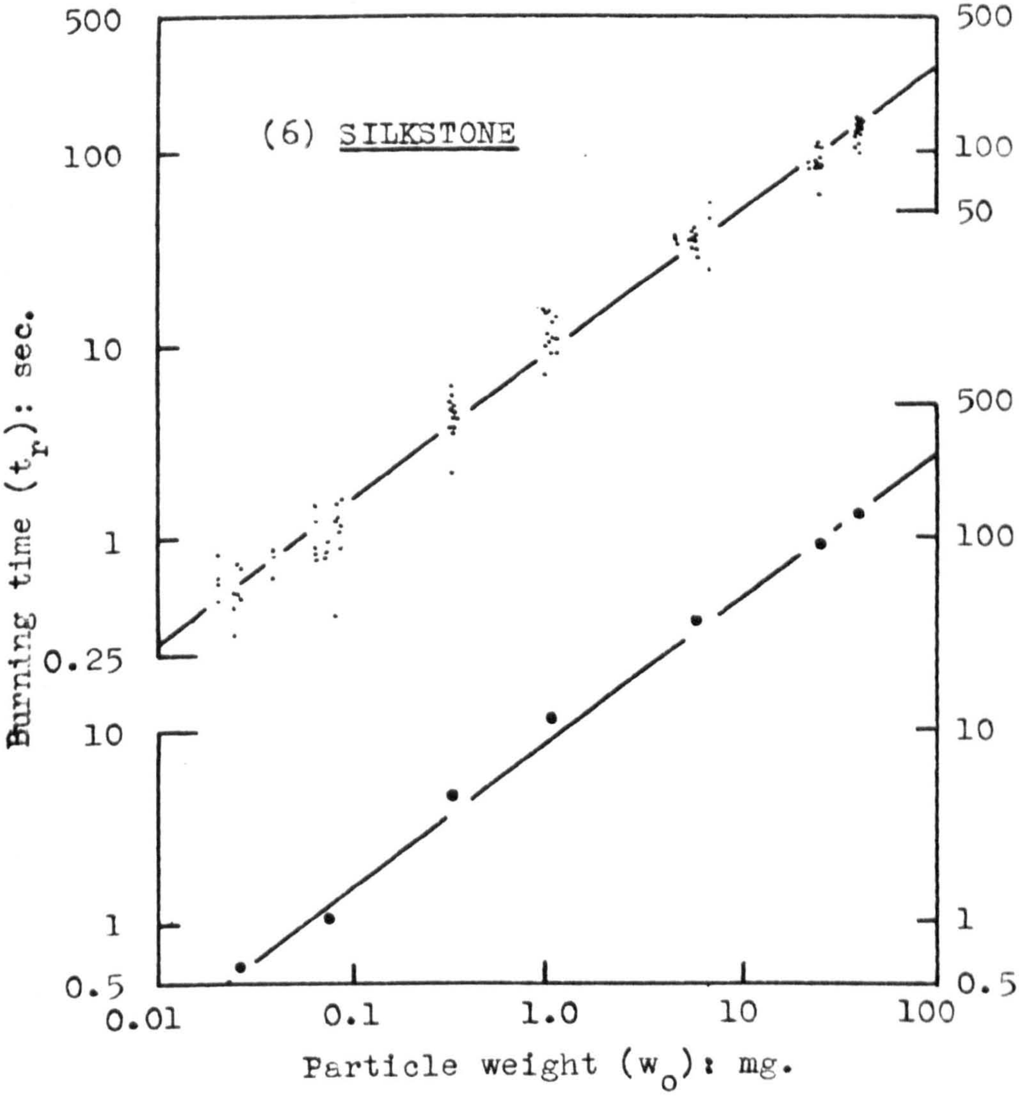


Fig. 8.6 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (102 points)

(Bottom) Averaged plot.

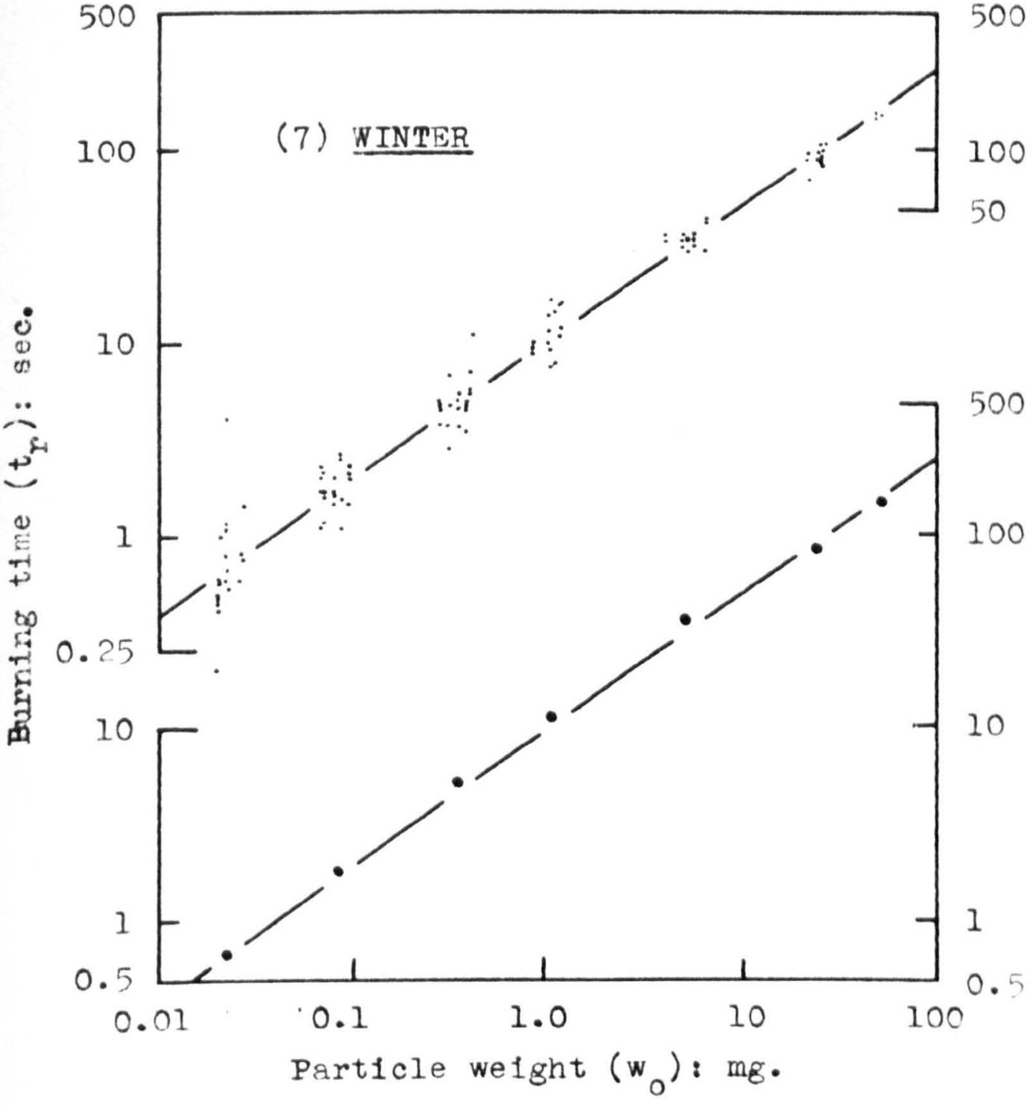


Fig. 8.7 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (105 points)

(Bottom) Averaged plot.

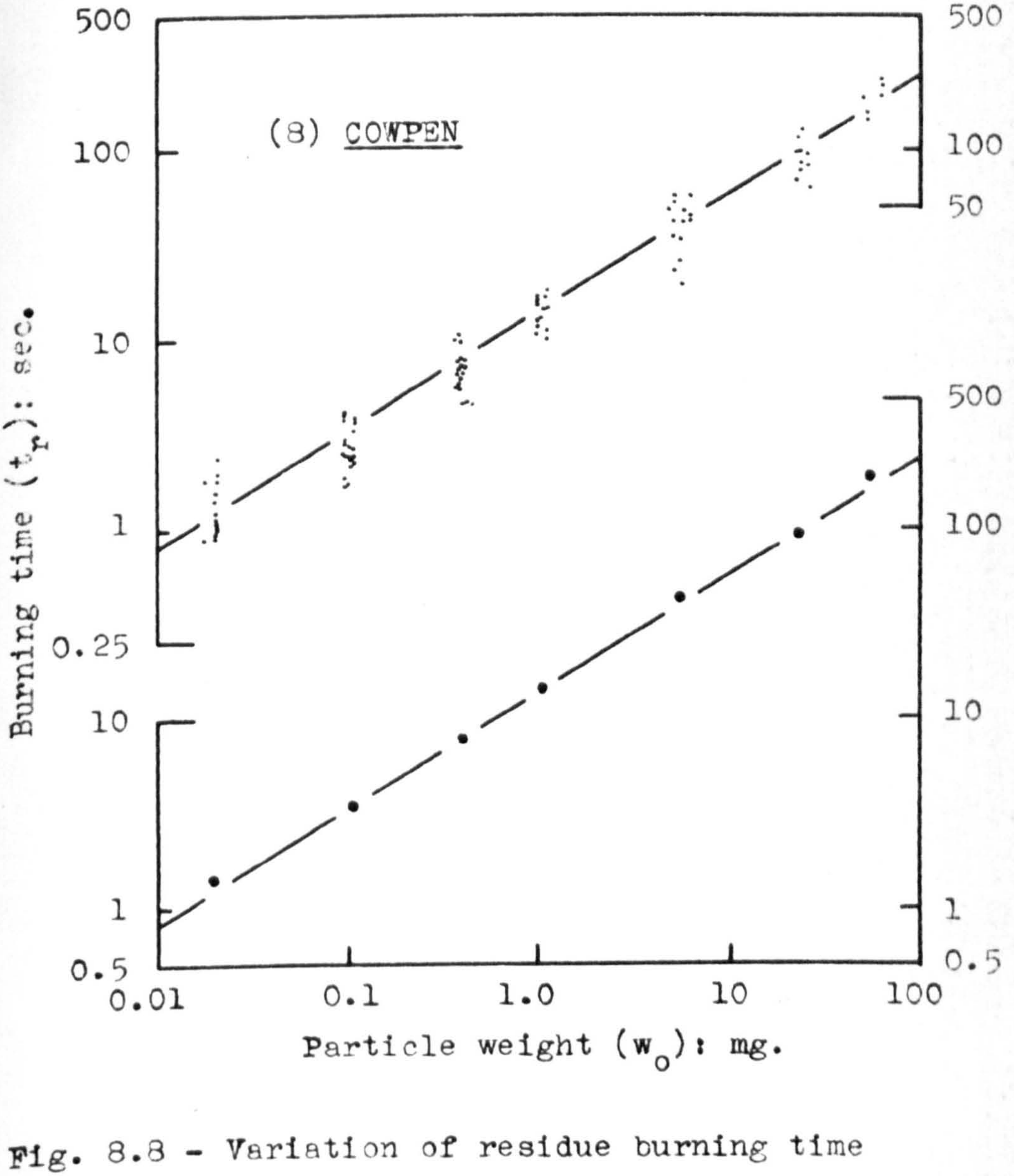


Fig. 8.8 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (98 points)
(Bottom) Averaged plot.

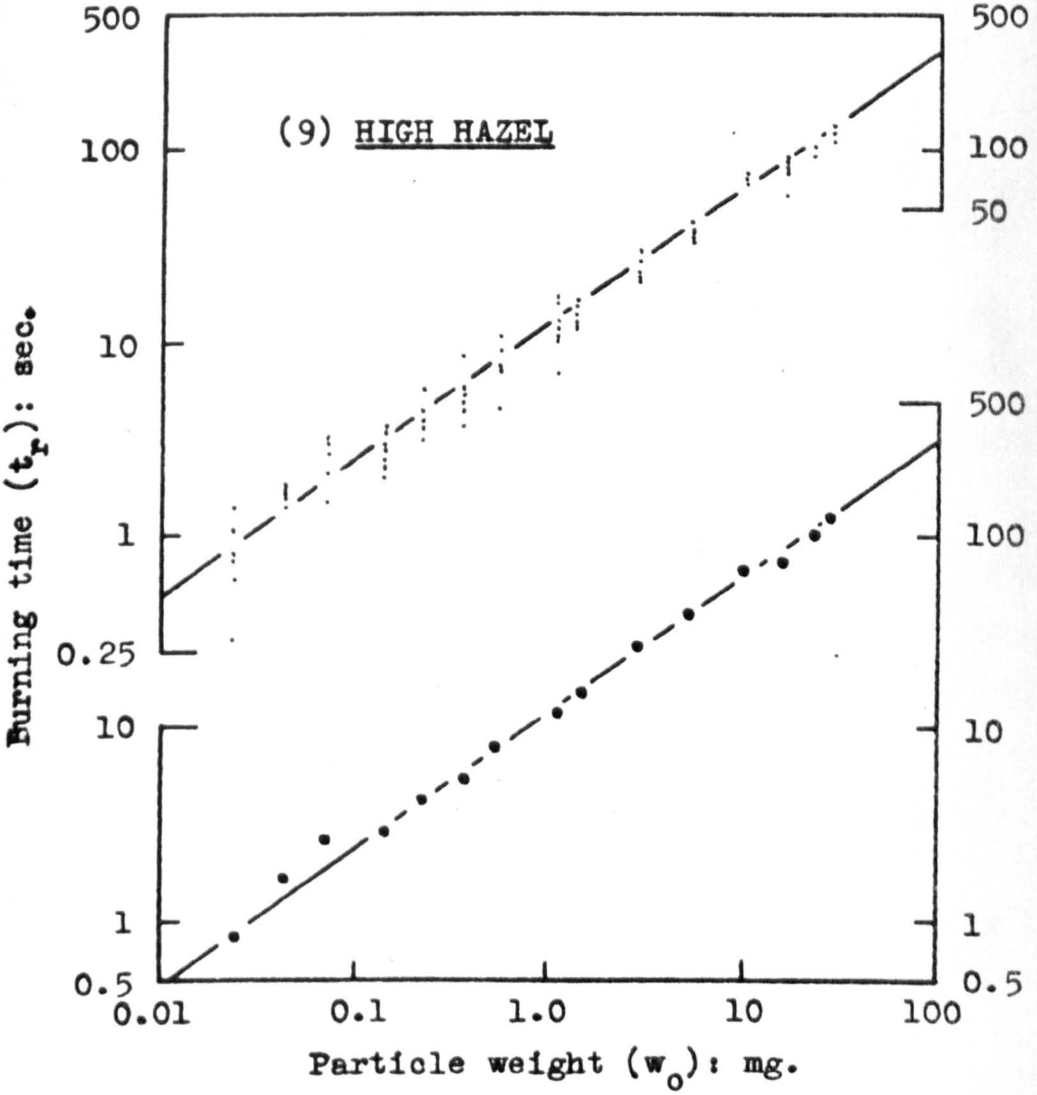


Fig. 8.9 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (75 points)
(Bottom) Averaged plot.

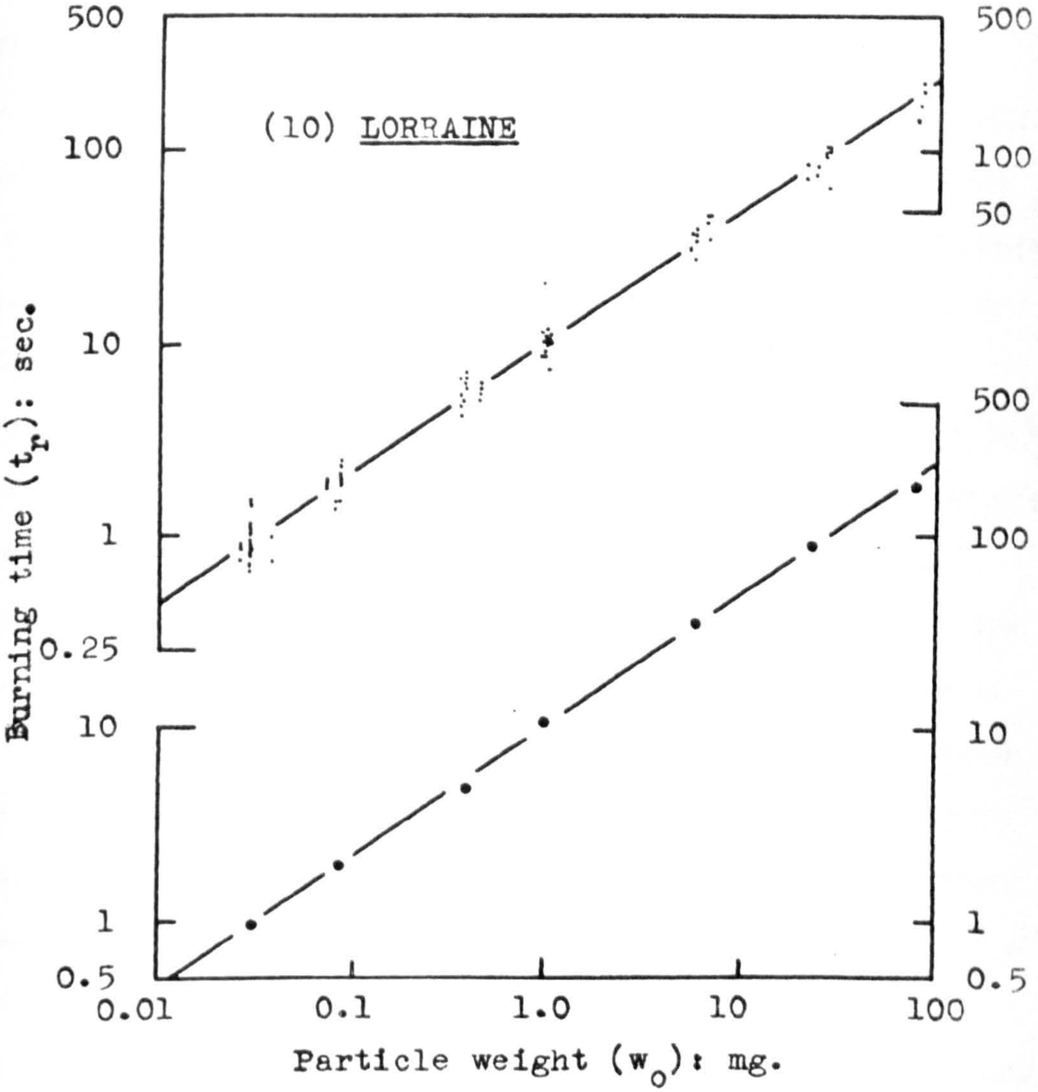


Fig. 8.10 - Variation of residue burning time with particle weight.

(Top) Scatter diagram (80 points)
(Bottom) Averaged plot.

and their values after conversion by equation (2) to the diameter basis (K_r and n_r) are given in Table 10b.

It is clear from the values of n_r in Table 10b that, for particles of this size burning under the conditions specified, the form of the reaction control is diffusional. Further support for this conclusion is provided by the order of magnitude comparison between the experimental values of K, listed as K_r, and their theoretical values, listed as K_D, calculated from equation (12) at a temperature of 1000° C after correcting for volatile loss; this correction for volatile loss was made by assuming loss of mass at the same particle diameter, i.e. at reduced density. In comparison, the values of the chemical burning constant K_c calculated from equation (15) are of the order of unity, a factor of 10^3 less than the experimental values. In view of the assumptions and approximations involved, the agreement between the experimental and calculated values is regarded as good, though it does seem from the calculated values of K derived by Spalding and Godsave (see Table 1) that the values are most insensitive to the detailed assumptions made. Even so, the agreement to within 50% shown in Table 10b can probably be improved upon if corrections are made for a number of neglected factors as follows:

TABLE 10.a

Experimental Values of Burning Constants for Residue Combustion

(Weight basis: c.g.s. units)

	Coal	%C (d.m.f.)	n_r'	K_r'
1	Stanllyd	93.0	0.659	2330
2	Five ft.	91.8	0.604	1290
3	Two ft. Nine	91.2	0.716	1330
4	Red Vein	89.7	0.695	1730
5	Garw	88.9	0.662	1470
6	Silkstone	86.9	0.750	1460
7	Winter	84.0	0.711	1270
8	Cowpen	82.7	0.614	1060
9	High Hazel	81.9	0.703	1510
10	Lorraine	79.3	0.674	1040

TABLE 10.b

Burning Constants for Residue Combustion (Diameter basis):

Comparison of Experimental and Calculated Values

(c.g.s. units)

	Coal	%C (d.m.f.)	n_r	K_r	K_D (Calc.)	Ratio K_D/K_r
1	Stanllyd	93.0	2.02	2125	2720	1.28
2	Five ft.	91.8	1.94	1290	2620	2.03
3	Two ft. Nine	91.2	2.25	1470	2070	1.41
4	Red Vein	89.7	2.09	1475	2275	1.54
5	Garw	88.9	2.01	1410	2030	1.44
6	Silkstone	86.9	2.25	1110	1655	1.49
7	Winter	84.0	2.18	1125	1710	1.52
8	Cowpen	82.7	1.94	1060	1775	1.68
9	High Hazel	81.9	2.14	1450	1725	1.19
10	Lorraine	79.3	2.20	992	1890	1.91

Mean Ratio: 1.55

(i) no correction was made for increased internal area due to the volatile loss, and hence increased reaction by internal burning. With diffusional control this may be a valid assumption.

(ii) the effect of swelling could not be corrected for as it was only observed visually and not measured. Its influence can be estimated on the basis of a density change to alter the density factor of equation (12). If the particles swell from diameter d_o to d_1, and the densities change from σ_o to σ_1 for no loss of mass (other than volatile loss already corrected for) we have

$$(\sigma_1/\sigma_o) = (d_o/d_1)^3$$

Now, if the residue had remained at its original diameter and density without swelling it would have burned out in a theoretical time t_o. At its new (unknown) diameter and density, it will be presumed to burn out in a theoretical time t_1 where, from equations (1) and (10) it follows that

$$\frac{t_1}{t_o} = \frac{(\sigma_1)}{(\sigma_o)} \cdot \frac{(d_1^2)}{(d_o^2)} = \frac{d_o}{d_1}$$

In the absence of quantitative knowledge of the behaviour of the particles on swelling we cannot say how d_o and d_1 are related but the most reasonable assumption is that each element of the solid structure swells by a constant amount so that

$d_1/d_o = f$, a swelling factor assumed constant.

If K_D is the theoretical constant calculated from equation (12), assuming no swelling, and K_r is the constant actually measured experimentally when t_1 is the measured burning time for an initial diameter d_o, then the parameters detailed above should be related as follows

$$t_1 = K_r . d_o^2 \text{ by definition of quantities}$$

$$= t_o/f = K_D . d_o^2/f$$

hence $K_r = K_D/f$

Since f is a factor in excess of unity (and thought to lie between 1.0 and 1.5) then taking this factor into account will reduce the theoretical values; that is to say, the correction will be in the right direction to improve the agreement between theory and experiment. We also see from the above relations that, if swelling is linear as suggested, we still have a square law relation between the burning time of the <u>swollen</u> particle and the <u>initial</u> diameter. Again, internal burning is neglected.

(iii) the presence of ash can influence the burning time in two ways: firstly by reducing the quantity of combustible material, so reducing the burning time; and secondly by providing an inert covering that, by screening the area available to attack by oxygen, will reduce this area and so increase the burning time. The first effect will be a function of the diameter cubed, and the second a function of the diameter squared; so the net effect should be an increase in burning time (reduced K) by a factor directly proportional to the diameter.

(iv) if the boundary layer is thinned sufficiently, this may also affect the reaction rate. Its possible influence may be estimated from equation (10a), though a precise treatment is not yet possible owing to lack of information of the behaviour of the boundary layer thickness δ with particle diameter under the conditions specified. We may however consider two special cases; (a) that δ decreases with radius, and as a first approximation has the dimensions of the fictitious film thickness (see Fig.5), so that $\delta = 2a$; and (b) that δ is constant, as when we might imagine it to be a volume bounded by the heating coils in these experiments, or else the boundary of the volume a particle is associated with in a P.F. flame.

(a) In the first instance, where we take δ (measured for mathematical simplicity from the particle centre) as j.a, where j is some factor greater than 1. Equation (1) then becomes

$$t_b = (1 - 1/j).K_D.d_o^2$$

In the case of the fictitious film, when j = 2, then the value of K_D is halved. If j is 10, K_D is still reduced by 10%. Clearly a turbulent aerodynamic field will have a marked effect on the value of K.

(b) In the second instance, for constant δ, equation (1) becomes

$$t_b = K_D.d_o^2.(1 - d_o/3\delta)$$

In general however the quantity $d_o/3\delta$ will be small, for instance in a P.F. flame (on the assumptions stated) the ratio would be about 0.01 so that K_D would be reduced by about 1% (though then dependent on diameter). However it is clear that more information on the behaviour of the boundary layer is required.

The various correction factors discussed above all tend to reduce the theoretical value of K though at present out knowledge is not sufficient for us to be able to apply quantitative corrections. Within those limits however the agreement between theory and experiment would seem to be quite reasonable.

6.4 Errors - The accuracy initially aimed at for the measured values of K, for the experiments planned and then carried out as described, was 5 to 10%, since this was considered quite adequate for these circumstances. This accuracy is believed to have been achieved.

Errors are of two sorts, random and systematic; if the accuracy of measurement is outside the 10% aimed at, this it is thought will be due to the systematic errors. Random errors are a nuisance in that they increase the number of tests required to achieve any stated accuracy; but systematic errors are the more important in that they are not counteracted by increasing the number of tests and so, if large, they can lead to totally erroneous conclusions.

On the random errors, the standard deviations in both n and K (Tables 8 and 10), calculated by the method of least squares, were under 5%, lying mostly between 2 and 3%. This was well within the original specification.

Of the systematic errors, these can be one of two types, or both together: a set of values can be subject to a zero error, so that all values are too large or too small by a constant amount; or they can be subject to a constant or varying scale factor. If the multiplying scale factor varies irregularly it can be regarded as a regular varying factor with a random variation superimposed, and the varying factor can then be represented by a power series.

Now in the relationship that was checked

$$t = K'.w^{n'}$$

we may assume that all the errors exist in the times and none in the weights. This is a reasonable assumption which is substantiated by the plots of Figs. 7 and 8, which show the scatter predominantly in the times. Now if we assume that the systematic error is a power function of the form $\Sigma s_r . t^r$, where the first (constant) term s_o is the zero error, then the real burning times can be obtained by equating this function with the nominal (measured) times. Making this substitution and then taking logs we get

$$\log(\Sigma s_r . t^r) = \log K + n.\log w$$

so that if the series function in time exists, the (logt/log w) plots of Figs. 7 and 8 would either be curved, or else the errors involved in creating curvature could be ignored. Since these plots show no marked curvature we are left with the two special cases that either: (1) only a zero error exists (i.e. $r = 0$); or (2) a simple power function exists (i.e. having only one term) when the equation above becomes

$$\log s + r.\log t = \log K + n.\log w$$

The possibility of a zero error existing was checked on the time/(weight)^n plots. The intercept at the origin on these plots is the zero error. This intercept was calculated in each case and found to be within twice its standard deviation (and generally better) so that any zero error existing was presumed to be not significant. There remains only the possibility of a power function error.

Possible sources of error are as follows:

(i) Random fluctuations in local ash concentration. This is clearly a random effect and is unlikely to introduce any systematic error.

(ii) Preferential size breakage of the petrographic constituents, thus giving perhaps large particles dominantly of durain, and the small one dominantly of vitrain (or vice versa). Having different combustion properties these could generate a scale error of the power function form.

(iii) Preferential shape breakage of the petrographic constituents, so that if one constituent breaks into cubes this will be chosen in preference to that breaking into needles. The error caused by this would be due to results being obtained on a selection of particles having an analysis differing from that of the average coal, so putting it out of place in the order of rank. Rank seems however to have less influence than expected.

(iv) Influence of the silica fibres and cement. The effect of this is difficult to estimate but the adverse effects of screening an area might be offset by the thermal capacity of the cement in maintaining the temperature at the end of combustion. The screening effect should not be overrated since frequently the larger particles burned away from under the cement and dropped off; also, on some occasions, with a medium ash coal the burning residue was held clear of the cement by a filligree tissue of ash. The effect will be partly random and partly, one would imagine, in the nature of a constant scale factor that would increase K_r.

(v) Finally there is the error in recording. The error of reading the records is clearly random; more important was the time base error due to variable chart speed. The speed was checked by timing marks at 1 sec. and 1/5 sec. intervals and corrections for deviations from the nominal stated speeds had to be made in four cases to the values of K calculated directly from the burning time values given in Tables 7 and 9. The values given in Tables 8 and 10 have been corrected where necessary by the following factors: Stanllyd, 1.065; Five ft., 1.09; Garw, 0.9375; and Silkstone, 1.02.

The total effect of all these errors is thought to be less than 10%, which is within the accuracy desired. Higher accuracy will not be worth while until either the theory can be improved or the necessary auxilliary measurements can be made for comparison.

7. DISCUSSION

As the underlying objective of this work was the elucidation of flame structure and mechanism, we must now consider to what extent this has been achieved; specifically we have to consider the validity of extrapolating these results to the range of smaller particle sizes found in P.F. flames, and to the different ambient conditions prevailing.

Over the size range examined the agreement between theory and experiment is reasonably good, and we can state with some confidence that, at this size range, the chemical resistance is negligible compared with the diffusional resistance. In extrapolating down to the P.F. size range it is therefore reasonable to expect that the same equations will operate, though modified to take into account the varying oxygen concentration found in a flame; but what we must also consider is the possibility of the chemical resistance changing less rapidly than the physical resistance as the particle size is reduced, with the possible consequence that the two become comparable at the smaller sizes, or even reverse in importance. In other words, are all the significantly relevant parameters still included in the extrapolation of the diffusion equations alone?

This consideration was prompted partly by some recent enquiries argued elsewhere (64,48), on the relative importance of the two resistances, and partly by a conclusion, to which Stewart (66) has recently drawn attention, of the result of a careful theoretical analysis by himself and Hottel (8) of reaction rates in P.F. flames using data then available. In this analysis the specific reaction rate was expressed as an inverse power function of diameter thus

$$R_s = C/d^m$$

where C was a constant, and m an index lying between 0 and 1 (see also sec. 5.2). Available experimental data were fitted to this equation to find the values of C and m for which the best fit was obtained. The significance of this operation will be clear from consideration of the contrasting equations (11) and (13) (secs. 5.1.4 and 5.2 respectively). As these equations show, the prediction from diffusional control is that the reaction rate is inversely proportional to the diameter (equation 11); but with chemical control, the reaction rate is independent of the diameter (equation 13). The value of m in the above equation may therefore be used to indicate the form of reaction control operating: $m = 1$, for diffusional control; and $m = 0$ for chemical. In the event, whereas Hottel and Stewart expected to find $m = 1$, they found m = 0. This they explained: either as a consequence of a high relative velocity for the larger particles; or else because the chemical resistance had a higher value than they had formerly anticipated. Between these two possibilities they do not seem to have made any specific choice, so leaving the question open; however, in the former case where relative velocity reduces the film thickness, there is then evidence that the chemical resistance is likely to be appreciable. The transit time (t_s) is the time required for a molecule to traverse a diffusion film of thickness δ, and for a flat plate is given (see Appendix) by

$$t_s = \frac{\delta^2}{2D_o}\left(\frac{T_o}{T}\right)^{1.75}$$

The residence time (τ) is the time a molecule will stay on a solid surface after being adsorbed, and before being desorbed again; this, according to de Boer (67) can be calculated from an equation due to Frenkel

$$\tau = \tau_o . \exp(+Q/RT)$$

where τ_o is a frequency factor that for carbon has a value of 5×10^{-14}; and Q is the heat of chemisorption of oxygen on carbon. The value of Q is uncertain but lies between 50 and 100 kcal., for instance Gulbransen and Andrew (68) have kept an oxide film on carbon at 575°C in a vacuum for several days without detectable loss in weight; by calculation from Frenkels equation this would indicate a heat of adsorption of 75 kcal. at least. These two times are direct measures of the respective resistances, and for comparison have been plotted together on Fig.9 for different values of Q and δ. At a value of 75 kcal. it is clear from this figure that the transit time at flame temperatures across a 100 micron film (this is the radius of a large particle) is significantly lower, or at least comparable with, the residence time; it does not become significantly greater until the temperature reaches about 2000^{o} C.

If this conclusion, that chemical resistance is still important at flame temperatures, is accepted, we now have to consider how this affects the calculation of burning times in a flame. Elsewhere (4) it has been shown that with diffusional control the burning time equation (1) is modified by the introduction of a factor F_D that takes into account the effect of the oxygen depletion through the flame. The modified equation may be written

$$t_b = F_D . K_D . d_o^2 \qquad (1a)$$

where

$$F_D = \frac{1 + E}{3E^{1/3}} \cdot f(E)$$

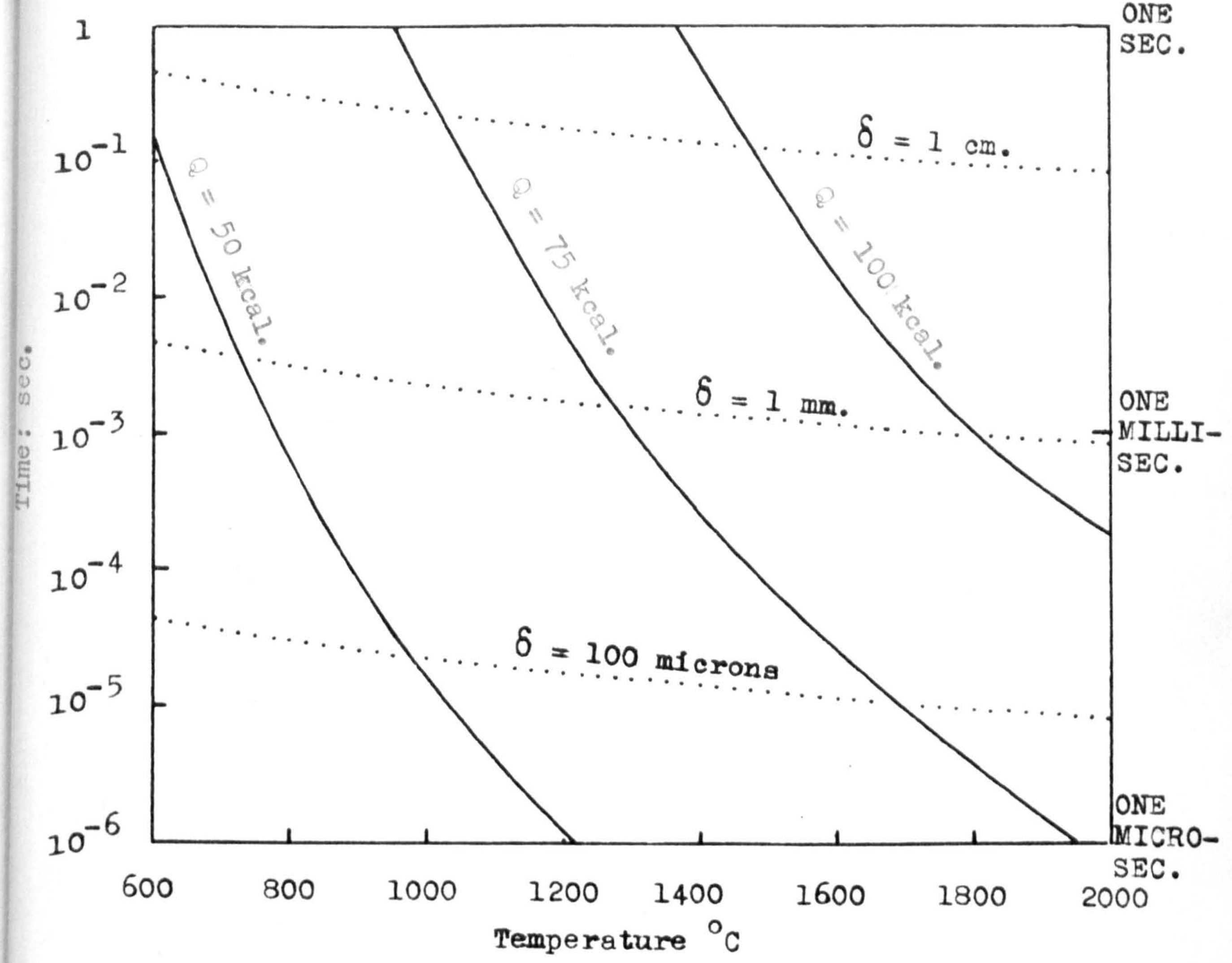


Fig. 9 - Variation with temperature of: (i) transit time (t_s) for an oxygen molecule diffusing to a solid surface through a film of thickness δ, and (ii) residence time (τ) for an oxygen molecule being adsorbed on a carbon surface with heat of adsorption Q.

· · · Values of transit time (t_s), for different δ

----- Values of residence time (τ) for different Q

$$\text{and} \quad f(E) = 2\sqrt{3}\tan^{-1}\left[\frac{\sqrt{3}}{2E^{1/3} - 1}\right] - \ln\left[\frac{(E^{1/3} + 1)^3}{E + 1}\right]$$

By a similar treatment of the chemical rate equation (13) we obtain a modified form of equation (14) which may be written similarly

$$t_b = F_c . K_c d_o \qquad (14a)$$

$$\text{where} \qquad F_c = \frac{1 + E}{2E^{2/3}} \cdot g(E)$$

$$\text{and} \quad g(E) = 2\sqrt{3}\tan^{-1}\left[\frac{\sqrt{3}}{2E^{1/3} - 1}\right] + \ln\left[\frac{(E^{1/3} + 1)^3}{E + 1}\right]$$

It will be seen that f(E) and g(E) differ only by the difference in sign between the two terms. The values of F_D and F_c have been calculated and plotted in Fig.10. Finally these graphs have been used to calculate t_b for different values of excess air from equations (1a) and (14a) for solid carbon in a flame at 1500° C, taking K_D as 1000 and K_c as 1, (calculated from equations 12 and 15). The values of excess air taken were 10%, 100% and infinity (i.e. the single particle), and the values are compared on a logarithmic plot in Fig. 11. These graphs show quite clearly that on the data taken the two resistances are comparable in an infinite atmosphere for a particle size of 10 microns. The size at which they are equal then rises as the excess air is reduced; at 10% excess air

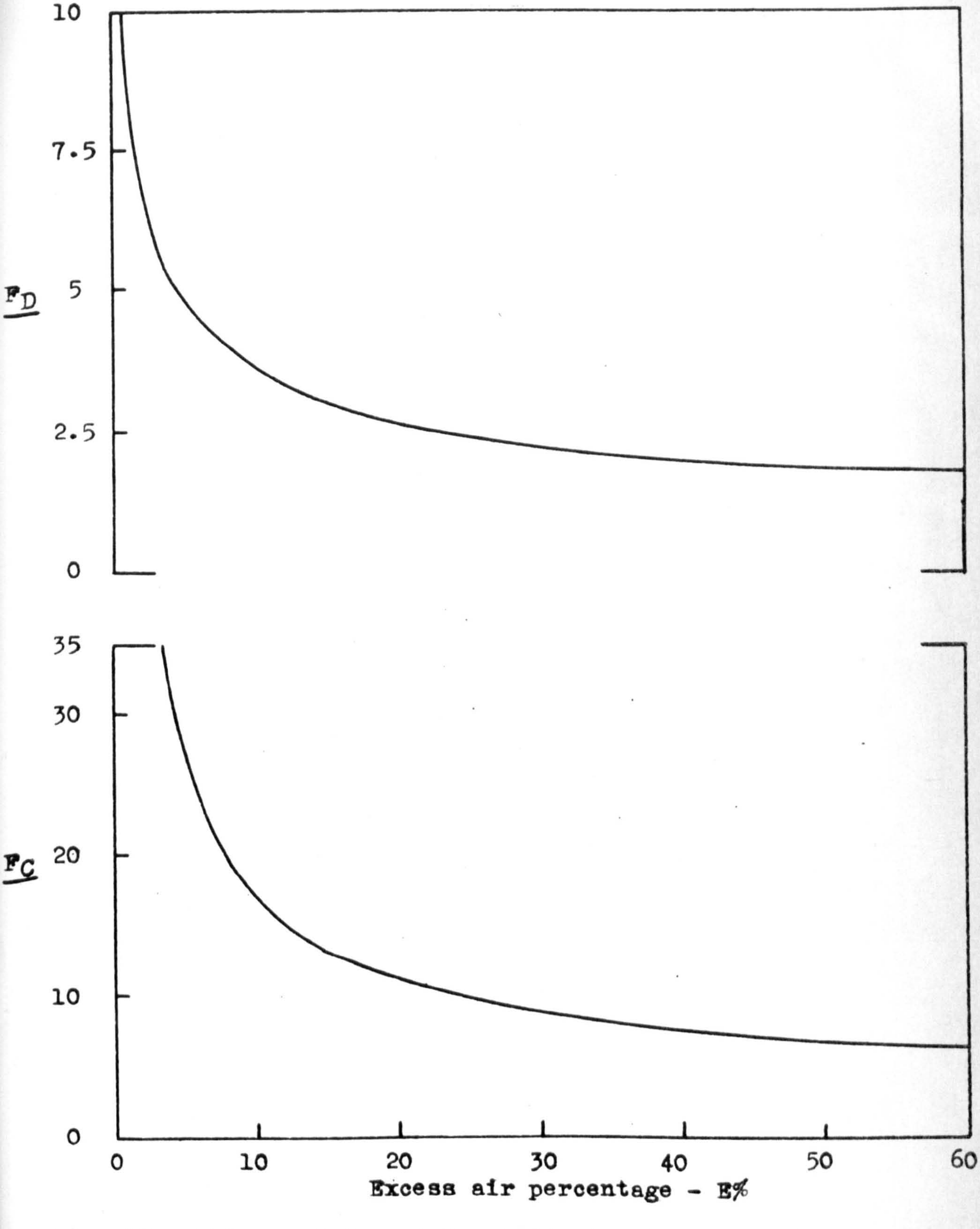


Fig. 10 - Values of F_D and F_C, diffusional and chemical multiplying factors for burning time in a flame, as functions of excess air.

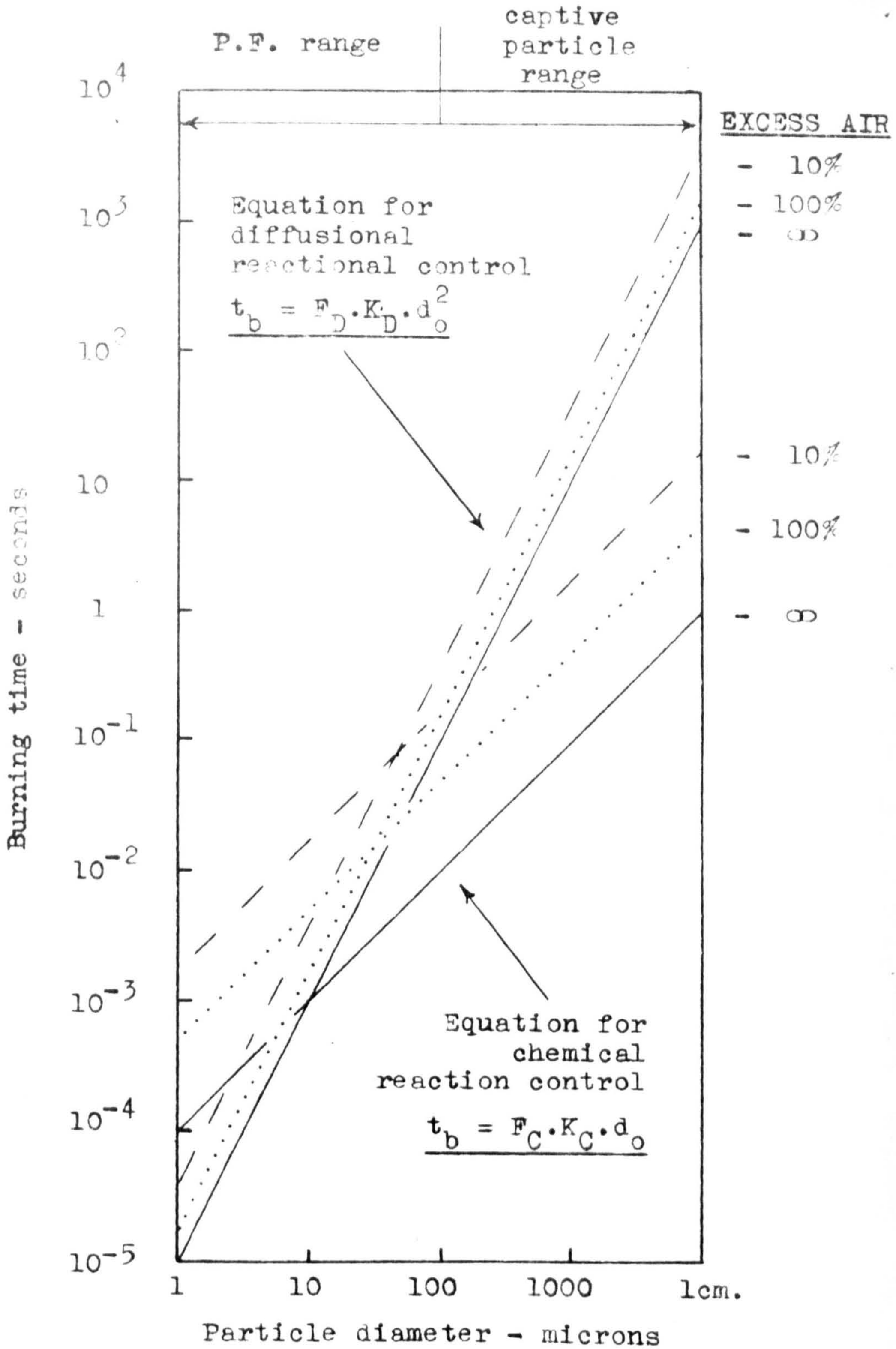


Fig. 11 - Comparison of calculated burning times in a flame, at 1500°C, on respective hypotheses of diffusional and chemical reaction control.

the two resistances are clearly comparable over the whole of the P.F. range with a tendency for the chemistry to dominate the process towards the smaller diameters, that is, as the particles burn out, in agreement with Khitrin's contention (69). The one possibly major factor not considered however is the effect on K_c of internal burning. If this is appreciable, as it may well be, it could so reduce the chemical resistance that the diffusion process still dominates the reaction. To determine whether or not this is the case would now seem to be the most important outstanding problem still awaiting solution in connection with the combustion mechanism of dust flames.

8. CONCLUSIONS

From what has been described and discussed in this thesis, the conclusions drawn are that:

(A) Experimentally -

1. The method of experiment described, by which captive particles of different coals in the size range 4 mm. to 300 microns were burned between a pair of heating coils, is a valid method of measuring the burning times of such particles.

2. The method of measurement, by which the radiation from the burning particles was picked up by a photocell and recorded, was sufficiently sensitive to distinguish between the characteristic volatile flame and the steadier residue combustion.

3. The accuracy of measurement of both volatile and residue burning times was sufficient.

(B) Theoretically -

1. The agreement between the experimental results on the residue combustion and theoretical predictions was good, the theory being based on the diffusion theory of reaction control predicting a square law relation between burning time of the residue (t_b) and the initial particle diameter (d_o)

$$t_b = K_D . d_o^2 \qquad (1)$$

where K_D is the burning constant.

2. The burning times of the volatiles also obeyed approximately a similar square law equation.

3. The accuracy of determination of the burning constants for both volatiles and residue was better than the ± 10% initially set as the limiting requirement.

4. The value of the burning constant for the volatile combustion (K_v) was about 100, which is of the order to be expected if the particle behaves during volatile emission as a pseudo liquid drop.

5. The predicted and experimental values of the burning constant for residue combustion (K_D and K_r) agreed to within an average factor of 1.5; the predicted values ranged from 1500 to 2500, and the experimental values ranged from 1000 to 2000. This agreement should be improved considerably if certain factors, such as swelling, that otherwise were ignored in the theory, were taken into account.

6. The predictions on the chemical theory of reaction control, that gave a burning time equation of the form

$$t_b = K_c . d_o,$$

were clearly unsubstantiated on two counts; firstly, that the predicted power of the diameter was unity, whereas that found experimentally was close to a square law as in equation (1) above; and secondly, that the predicted value of K_c was about unity, whereas that found experimentally (and predicted by the diffusion theory) was a factor of more than 1000 greater.

7. Nevertheless, with decreasing particle size, even at $K_D = 1000$ and $K_c = 1$ (calculated for 1500°C), the predicted burning times (and therefore the two resistances) become comparable at a particle size of 10 microns.

8. Furthermore in a flame, with the introduction of the flame multiplying factors F_D and F_c (that are function of excess air alone and that take into account the depletion of oxygen through the flame), the particle size at which the burning times become comparable increases as the excess air decreases. The general predictions are that in real flames the two resistances may well be comparable over the whole of the P.F. range.

(C) <u>For Future Work</u> -

1. The technique as it stands offers some scope for improvement of accuracy, but this would be a waste of time unless the additional parameters of swelling, shape factor, ash effect and variation of the boundary layer are taken into account to improve the agreement between theory and experiment.

2. Two outstanding laboratory problems shown up by this work are

(i) the need for better knowledge of the influence of the boundary layer, for example, by repeating the experiment with varying velocity and particle size.

(ii) the need to check: (a) that the volatile combustion time is independent of oxygen concentration (provided there is still sufficient oxygen for combustion); and (b) that the residue reaction at flame temperatures is in fact first order with respect to the oxygen concentration.

3. A further laboratory problem, revealed partly by this work and partly by work on flames, is the need (as originally visualised) to investigate the differential effect of heating by convection and by radiation.

4. There is a clear need for more accurate, and unambiguous, data on the combustion rates in a flame so that the controlling mechanism of the reaction can be elucidated. There is some hope that this data may be supplied by the new furnace just built and designed to generate a one-dimensional flame.

9. LIST OF SYMBOLS

a;	particle radius
d;	particle diameter
d_o;	initial particle diameter
D, D_o;	diffusion coefficient at temperatures T and T_o respectively
E;	activation energy of chemisorption ; fractional excess air
E%;	percentage excess air
f;	swelling factor
F_D, F_C;	diffusional and chemical multiplying factors for burning times in a flame (functions of excess air)
G;	rate of transport of oxygen to a solid surface by diffusion
G_s;	value of G at solid surface
K;	burning constant
K_D, K_C;	theoretical values of K predicted by diffusional and chemical hypotheses of reaction control respectively
K_v, K_r;	experimental (measured) values of K for volatile and residue combustion respectively
K'_v, K'_r;	values of K on a weight basis
L_s;	characteristic length in diffusion equations
M;	constant of proportionality (experimental) in weight/diameter equations; total number of molecules per c.c. at normal pressures
M_o;	mean molecular weight of diffusing gas mixture
m;	index in weight/diameter equations
N;	number of molecules of oxygen per unit volume

N_o, N_s;	values of N in main stream and at solid surface respectively
n;	index in burning time/diameter equations
n_v, n_r;	values of n for volatile and residue combustion respectively
n'_v, n'_r;	values of n on weight basis
p;	oxygen partial pressure
p_o, p_s;	values of p in main stream and at solid surface respectively
Q;	heat of chemisorption
R_s;	specific reaction rate of carbon (gm/unit area/sec)
R;	gas constant
r;	radius - distance from particle centre
t_b;	burning time (sec)
t_v, t_r;	experimental values of t_b for volatile and residue combustion respectively
t_s;	transit time for an oxygen molecule crossing the diffusional boundary layer
T;	temperature
T_o	standard temperature
v;	diffusional convective velocity
v_s;	values of v at solid surface
w_o;	initial weight of a particle
δ;	diffusional boundary layer thickness
ρ;	gas density
σ;	particle density
τ;	residence time of an oxygen molecule on a carbon surface

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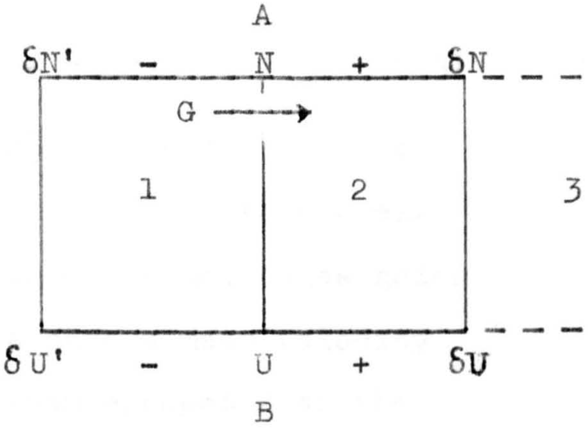
APPENDIX

Derivation of Equation for Transit Time Across a Diffusional Boundary Layer

Fluid molecules diffusing through a second fluid travel at a net (average) drift or diffusional velocity, U, which can be shown to be a function of both concentration and of the concentration gradient.

Consider a plane AB in the yz plane sited at x, with volume elements 1 and 2 of volume $\delta V'$ and δV respectively. Their common face is an area $\delta y.\delta z$. At the plane AB, the concentration and drift velocity of the diffusing fluid is N and U; at the element boundaries i.e. at $(x - \delta x')$ and $(x + \delta x)$ they are respectively $(N - \delta N')$, $(U - \delta U')$ and $(N + \delta N)$, $(U + \delta U)$:



The numbers of molecules in elements 1 and 2 are therefore;

In 1: $(N - \delta N'/2).\delta V'$; and in 2: $(N + \delta N/2).\delta V$

As the net effect of diffusional exchange between all volume elements, we may take it that, of the molecules in element 2, half go to element 1 and half to element 3; similarly for element 1. The net exchange per unit area per sec, across the plane AB is therefore given by

$$G = \tfrac{1}{2}(N - \delta N'/2)\delta V'/\delta y.\delta z.\delta t - \tfrac{1}{2}(N + \delta N/2)\delta V/\delta y.\delta z.\delta t$$

$$= \frac{N}{2}\left[\frac{\delta x'}{\delta t} - \frac{\delta x}{\delta t}\right] - \frac{\delta N'}{4}.\frac{\delta x'}{\delta t} - \frac{\delta N}{4}.\frac{\delta x}{\delta t} \qquad (A1)$$

But $\delta x'/\delta t$ is the mean drift velocity of the molecules in element 1 so that

$$\delta x'/\delta t = U - \delta U'/2 \qquad (A2)$$

Similarly for 2:

$$\delta x/\delta t = -(U + \delta U/2) \qquad (A3)$$

The negative sign in equation (A3) appears since the motion of the molecules in element 2 going to element 1 is in the -x direction, and since the molecules going from element 2 to element 3 then have a mean velocity $+(U + \delta U/2)$, the momentum lost from element 2 as the molecules leave is zero.

Substituting for $\delta x/\delta t$ and for $\delta x'/\delta t$, we have

$$G = N.U - \tfrac{1}{4}.\frac{\partial}{\partial x}(NU).(\delta x' - \delta x)$$

$(\delta x' - \delta x)$ is in any event small, but in the limit as δx and $\delta x'$ tend to zero, this term vanishes leaving

$$G = N.U \qquad (A4)$$

Since $$dx = U.dt$$

the transit time is given by

$$t_s = \int_0^\delta \frac{dx}{U} = \int_0^\delta \frac{N.dx}{G}$$

The standard equations for the case of diffusion to a plane give us

$$N = N_o(1 - x/\delta)$$

and

$$G = D.N_o/\delta$$

where N_o is as before the main stream concentration, and the surface concentration N_s is taken as zero.

Substituting for N and G, and integrating between the limits given, the solution obtained is

$$t_s = \delta^2/2D \qquad (A5)$$

$$= \frac{\delta^2}{2D_o}\left(\frac{T_o}{T}\right)^{1.75}$$

the relation $D = D_o.(T/T_o)^{1.75}$

being taken from International Critical Tables 5 (1929) 62.

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