

THE INFLUENCE OF OXYGEN CONCENTRATION ON DUST EXPLOSIBILITY

C.G. Sinclair and F.K. Sweis*

Information on the maximum permissible oxygen concentration to prevent ignition in a dust cloud, y_o^m , is presented for a variety of industrial and pure chemical dusts. Measurements were made in a modified version of the standard small vertical tube apparatus used for dust explosibility tests. The minimum ignition temperature in air, T_i^m , for the same dust was measured in the furnace apparatus. Further work on the effect of oxygen concentration on the maximum explosion pressure, P_{max} , and the maximum rate of pressure rise, $\left(\frac{dP}{dt}\right)_{max}$, is also reported. These measurements were made in a modified Hartmann bomb. In all cases the diluent gas was nitrogen. The only useful correlation for y_o^m arising from the work is that between the maximum oxygen concentration to prevent ignition and the stoichiometric concentration of dust in air. The relationship between the maximum explosion pressure and the maximum rate of pressure rise at any oxygen concentration was found to be consistent between one material and another, and it is shown that knowledge of P_{max} , $\left(\frac{dP}{dt}\right)_{max}$ and y_o^m allows conservative estimates of the explosion pressure to be calculated for any oxygen concentration.

INTRODUCTION

Dust explosions are a continuous hazard both to personnel and property in processes which involve fine combustible powders. One of the methods of preventing a dust explosion is to dilute the dust atmosphere with inert gases such as nitrogen.

A fundamental theory explaining the initiation and continuation of a dust explosion is not yet available, and this is attributed to the difficulty of modelling the initiation of a dust explosion(1).

The maximum permissible oxygen concentration at which a dust explosion will not occur is an important parameter for the design of inerting systems but its measurement is a time consuming procedure. It would be useful if this parameter could be correlated with more easily measured properties of the dust such as the heat of combustion, and the kinetic and stoichiometric parameters of the combustion process. The experimental work reported in this paper was undertaken as a step in this direction. Data on the maximum permissible oxygen concentration to prevent ignition and its variation with the dust concentration, and the behaviour of maximum explosion pressure and maximum rate of pressure rise in a controlled oxygen atmosphere are presented for a variety of dusts.

Previous Work

The standard small scale furnace apparatus is in current use for measuring the maximum permissible oxygen concentration to prevent dust explosions(2).

* Department of Chemical Engineering, UMIST, Manchester, England.

This test has been criticised by many workers in the field(3,4,5,6). It has been suggested that the furnace test gives unnecessarily low oxygen values, and hence higher inerting costs, for many industrial processes, particularly for those industrial plants which excluded large sources of ignition comparable to that of the furnace test(5).

Craven and Foster(4) compared results obtained from the furnace apparatus to those obtained with a large scale vertical tube apparatus. They found that the furnace apparatus gave lower values than the large scale vertical tube apparatus, they also found that the maximum permissible oxygen concentration varies with the temperature of the apparatus.

Tonkin and Fardell(3) investigated the possibility of establishing a small scale apparatus to give results applicable to industrial purposes. The small scale vertical tube apparatus used for standard dust explosibility measurements was found to give similar results to the large scale vertical tube apparatus mentioned above. It was therefore suggested that this would be an appropriate test for maximum permissible oxygen concentration.

Nagy et al (7) studied the behaviour of the maximum explosion pressure and maximum rate of pressure rise when the oxygen concentration is reduced below that in air. They found that the maximum explosion pressure reduced slowly as the oxygen concentration slightly reduced, but as the limiting oxygen concentration was approached, the maximum explosion pressure decreased at a more rapid rate. The maximum rate of pressure rise decreased almost linearly with decrease in oxygen concentration.

Materials

The chemical dusts which were used in this work are listed in Table 1 together with the moisture content of each. All the dusts were of the same particle size - 90 + 75 μ m.

Table 1, Materials

Material	Moisture Content %
Benzoic Acid	3.8
Diphenylol Propane*	0.53
(+)-Tartaric Acid	0.21
Sucrose	0.17
ABS Copolymer**	0.52
Citric Acid	0.15
Glutamic Acid	0.13
Glutaric Acid	-
Napthalene	-

* Bisphenol A; 4,4 - Isopropylidenediphenol

** Acrylonitrile(18.9%) Butadiene(14.6%) Styrene(64.6%)

Equipment

The maximum permissible oxygen concentration, maximum explosion pressure and maximum rate of pressure rise in a controlled oxygen atmosphere were measured in a modified version of the small vertical tube apparatus and the Hartmann bomb respectively. Both of these in their unmodified form are standard test items described by Raftery(2). A diagrammatic form of the modified

versions are shown in Figure 1 and Figure 2.

The source of ignition in both apparatus was a continuous electric spark, and nitrogen was used as the inert gas.

The general principle of each modification was to fill the apparatus with the required gas mixture. Air and nitrogen were mixed and were analysed by an oxygen analyser (Teledyne Analytical Instruments Type 320B) in order to measure the oxygen content of the gas mixture. The metered gas mixture after passing through the oxygen analyser and a pulsation damper was either used at low pressure for purging, or compressed into the gas reservoir for dust dispersion in the usual way.

The purging line in the small vertical tube apparatus was connected to the explosion tube just above the dispersion cup. With the Hartmann bomb, it was connected to the main line at a point between the full port solenoid valve and the non-return valve, another non-return valve was incorporated into this line.

In the Hartmann bomb, a small valve was fitted to the top of the explosion tube to permit the purging gas to emerge. The top of the explosion tube was also fitted with a Bell and Howell pressure transducer (type 4-366-0001-03M0) the output from which was fed to an amplifier and storage oscilloscope (Tektronix type 654) so that a pressure time record of the explosion could be obtained. Oscilloscope traces were photographed and enlarged to obtain measurements.

A filter paper diaphragm with a small hole in the centre (0.5 cm) was attached across the top of the vertical tube apparatus.

The oxygen analyser flow cell could be moved from the inlet to the outlet at the top of the explosion tubes in order to check that the purging was complete.

The standard furnace apparatus(2) was used to measure the minimum ignition temperature of the dusts.

Procedure

The procedure carried out in both explosion tubes was as follows;

1. When the desired oxygen concentration had been achieved, the gas reservoir was emptied and refilled three times and then charged up to the desired dispersion pressure.
2. A weighed quantity of the dust was placed in the dispersion cup of the apparatus.
3. The gas mixture was allowed to flow through the explosion tube at a rate of about 5 litre/min until the outlet concentration was the same as the inlet.
4. The ignition source was energised.
5. The full port solenoid valve was opened, and the dust was dispersed by a blast of the air/nitrogen mixture.

The criterion for indicating an explosion in the small vertical tube apparatus was the propagation of flame away from the ignition source; full

flame propagation was usually accompanied by bursting of the filter paper diaphragm. When an explosion occurred, the oxygen concentration was reduced and testing was continued until no explosion was observed in three tests at the same dust concentration.

If no explosion occurred at the first attempt, further attempts were made to explode the dust by varying the pressure of the air/nitrogen mixture (40-50 lb/in²) and/or varying the gap between the electrodes (0.5-1.0 cm)

The dust concentration which was chosen for the experiments carried out in the Hartmann bomb was that which gave the highest maximum explosion pressure in air for that particular dust. The dispersion pressure was 120 lb/in².

Technique

As the results of explosion tests usually depend on the skill of the operator, it was necessary to compare our values with those reported by other workers.

The $y_{O_2}^m$ value for diphenylol propane found in this work was 12% whereas a value of 9.8% has been reported(3) for the same material, but with a mean particle diameter of 133 μ m and a moisture content of 0.6%(6).

In order to obtain a value in reasonable agreement to that reported in the literature, it was found necessary to reduce the particle size of the dust from - 90 + 75 μ m to - 45 μ m. The value obtained was 8.8%. Figure 3 compares the literature results obtained for diphenylol propane having a mean particle diameter of 122 μ m with those obtained by us for a particle size of 45 μ m.

Table 3 compares our measurement of $(P)_{max}$ and $(\frac{dP}{dt})_{max}$ in air and T_i^m values, to those reported in the literature. The values obtained were in good agreement.

Table 2

Comparison of the Measurements

No	Material	(P) max in air (psi)		$\frac{dP}{dt}$ max in air (psi/s)		T_i^m °C		Reference
		This work	Literature	This work	Literature	This work	Literature	
1	Benzoic Acid	99	85	10000	10300	630	600	2
2	Diphenylol Propane	83	81	10500	11800	550	570	2,8
3	Sucrose	87	93	1307	2100	440	420	2,8

RESULTS AND DISCUSSION

Maximum Oxygen Concentration to Prevent Ignition ($y_{O_2}^m$)

Figures 4 and 5 show the variation of $y_{O_2}^m$ in per cent by volume with dust concentration g/l, for benzoic acid and glutamic acid respectively. Each point

on the graphs represent a group of three tests in the vertical tube apparatus and where the extent of flame propagation varied within a group, the point shown represents the most extensive flame propagation.

In the present study, a distinction is made between flames propagating the full tube length (usually accompanied by bursting the filter paper diaphragm), those propagating part tube length, and no propagation at all (i.e. no flame propagated away from the ignition source).

In Figure 4, it can be seen that as the dust concentration of benzoic acid increased from 0.03 g/l to 0.06 g/l, y_{O^m} dropped sharply from 16% to 9%, and the critical oxygen value of 8.5% was approached when the dust concentration increased to 0.1 g/l. A further increase in the dust concentration resulted in a slow increase of the oxygen concentration.

The pattern for glutamic acid, Figure 5, was somewhat different showing a shallow minimum with the critical value of 13% being reached at a dust concentration of 1.5 g/l. A further increase in the dust concentration resulted in an increase in y_{O^m} . Both curves show a well defined y_{O^m} .

Figure 6 and 7 summarise the results for all the materials investigated. In general, each shows a well defined minima which is taken as the maximum permissible oxygen concentration to prevent ignition. At oxygen concentrations above the maximum permissible for preventing explosion, flame propagation is possible (full tube and part tube), and below the maximum permissible, flame propagation is not possible.

In general, the aromatic compounds (benzoic, naphthalene, ABS co-polymer and diphenylol propane) tend to give lower values of y_{O^m} than the aliphatic compounds.

The maximum permissible oxygen concentration occurred at a dust concentration at or near the stoichiometric concentration for naphthalene, glutamic acid, glutaric acid and citric acid, but higher than the stoichiometric concentration with ABS co-polymer, diphenylol propane and sucrose, and lower with benzoic acid and tartaric acid.

Values of y_{O^m} and the corresponding dust concentration at which they were obtained, together with the stoichiometric concentrations of the materials in air, are shown in Table 3.

As mentioned previously, one aim of this work was to begin the process of establishing correlations for y_{O^m} in terms of other parameters. The main theoretical treatment of relevant combustion phenomena is based on equating heat release rates in the flame to heat loss rates from the flame to the surroundings. Heat release rates might be expected to depend on the nett heat of combustion (since the phenomena is over before condensation of water vapour occurs) and the reaction rate. Heat loss rates may depend on the incandescence of the dust particles and their surface area concentration etc. as well as equipment factors. The reaction rate in turn will depend on the oxygen and dust surface concentrations, the surface properties of the dust and the chemical structure.

The experimental data is too sparse at the moment to warrant complex treatments and we have limited this work to one or two empirical correlations. These will of necessity lead to some false conclusions but as more data becomes available the situation will improve.

All the compounds tested were in the same standard sieve range between 75 and 90 μm aperture. The parameters which we considered might be relevant for correlation and which we could measure were:-

Nett heat of combustion, ΔH_C
 Maximum pressure and maximum rate of pressure rise in air, which we thought might be related to reaction properties.
 Actual dust concentration at y_0^m (x_0^m g/l)
 Stoichiometric dust concentration in air (x_2 g/l)
 Minimum ignition temperature (T_i^m $^{\circ}\text{C}$)

Quantities derived from the above parameters which we also thought might be useful were:-

A measure of the reaction time of the dust explosion $t_r = \frac{P \text{ max}}{(dP/dt) \text{ max}}$

A measure of the maximum heat release in a dust explosion in air

$$\Delta H_{CV} = \frac{x_2 \Delta H_C}{M} \text{ kcal/litre}$$

and

A measure of the maximum rate of heat release at the actual dust concentration

$$\frac{x_0^m \Delta H_C}{M t_r} \quad \frac{\text{kcal}}{\text{g s}}$$

where M is the molecular weight of the material.

The values of these various quantities are listed in Table 3 for the nine compounds tested in order of decreasing y_0^m .

The only realistic conclusion that can be drawn from this table is that y_0^m is dependent on the stoichiometric dust concentration in air. This is plotted in Figure 8, where we have drawn the curve to leave diphenylol propane as the odd point out. Comparing this compound with the others in Table 3, we note that it has the fastest reaction time and the highest (though only by a small margin) heat of combustion. We cannot explain this correlation which may, of course be purely fortuitous. It is our intention to check the correlation for highly reactive and unstable compounds and for the types of mixtures and formulations common in industry.

So far as the other parameters are concerned little can be said other than that low values of y_0^m tend to be associated with low reaction time, high nett molar heats of combustion and high maximum rates of pressure rise. The minimum ignition temperature which was determined in the furnace apparatus seems to be a completely meaningless parameter. This equipment in which this parameter is measured has been criticised on other grounds and would seem to be ripe for replacement.

We have already mentioned the apparent split between aromatic and aliphatic compounds and it may well turn out that each class of compounds has its own individual correlation.

It was disappointing that the dust concentration at which y_0^m occurs is unrelated to the stoichiometric concentration of the dust in air or in the air/

nitrogen mixture whose oxygen concentration is y_o^m .

Maximum Explosion Pressure and Maximum Rate of Pressure Rise in a Controlled Oxygen Atmosphere

Figure 9 shows a standard curve for the variation of pressure with time for any dust (8,9). The small initial pressure rise P_1 is due to entry of the dispersing gas into the explosion tube. Frequently, with dusts having a high maximum explosion pressure, P_1 does not appear and pressure rises from the beginning of the test. The rise in pressure is due to the combustion of the dust and it commences after the entry of the dispersing gas into the explosion tube. P_2 is the maximum explosion pressure of the dust.

The method of calculating the maximum explosion pressure P_{max} from a pressure-time record was

$$P_{max} = P_2 - P_1$$

and the maximum rate of pressure rise was calculated from the gradient (a/b).

Figures 10, 11, 12 and 13 show the variation of the maximum explosion pressure and the maximum rate of pressure rise with the oxygen concentration in per cent by volume, for benzoic acid and sucrose respectively. They are representative of the results obtained. Several experiments were carried out at each oxygen concentration, and each point on the graphs represent one experiment. The maximum explosion pressure and maximum rate of pressure rise were taken as the highest values obtained with each oxygen concentration.

As can be seen from Figures 10 and 11, as the oxygen concentration is slightly decreased below that in air, the maximum explosion pressure of benzoic acid is slightly decreased, whereas the rate of pressure rise drops rapidly. A further decrease in the oxygen concentration has a large effect on the maximum explosion pressure and a lesser effect on the rate of pressure rise.

The behaviour of sucrose, Figures 12 and 13, is somewhat different, in that the maximum explosion pressure and maximum rate of pressure rise are both almost linearly related to the decrease in oxygen concentration.

Figures 14, 15 and 16 summarise the results for all the materials tested. Tartaric acid does not appear since it did not explode in the Hartmann bomb. The dust concentration corresponding to each curve is listed in the legend and is that which gives the highest maximum pressure in air.

In general they show the same pattern as the sample curves and extrapolate to values of oxygen concentration at zero pressure which are very close to those determined in the vertical tube apparatus at the same dust concentration (cf Figures 6 and 7).

The similarity in shape of the curves suggests normalisation. This has been done in Figures 17 and 18 where

$$\frac{P_o^m}{P_{21}^m} \quad \text{and} \quad \frac{(dP/dt)_o^m}{(dP/dt)_{21}^m} \quad \text{have been plotted as ordinates with}$$

$\frac{y_o - y_o^m}{y_{21} - y_o^m}$ as abscissa.

The subscript, 21, indicated the value in air and the subscript 0 refers to a particular oxygen concentration. Although there is some scatter in the data points (which have been taken from the summary curves Figures 14, 15 and 16) we have drawn conservative curves through the points.

A good estimate of the maximum explosion pressure at any oxygen concentration can be obtained from Figure 17 knowing only the maximum pressure in air and the value of y_o^m . This information is obviously of value in choosing an oxygen concentration in the atmosphere where the equipment can withstand pressures higher than atmospheric.

Similarly, for rate of pressure rise estimates which are of importance for vent design, the solid line in Figure 18 can be used. However as indicated by the dashed curve, aromatic materials give a much greater reduction in the maximum rate as the oxygen concentration is lowered and hence for these materials the estimate would be over conservative.

CONCLUSIONS

The experimental data presented for y_o^m , P_{max} and $\left(\frac{dP}{dt}\right)_{max}$ in a controlled oxygen atmosphere provide comprehensive information for assessing the hazards of many combustible dusts.

By analysing the data obtained, it has been possible to obtain two results which may prove to be useful in plant design purposes.

1. The dependence of y_o^m on the stoichiometric dust concentration in air.
2. The estimation of P_{max} and $\left(\frac{dP}{dt}\right)_{max}$ at any oxygen concentration.

The y_o^m values reported did not include a safety factor. In applying these values to industrial purposes, a safety factor must be used to allow for fluctuations in the oxygen concentration.

The tests carried out in this work were only related to the ignition of dust clouds, and do not relate to dust layers which in case of fire may continue to burn at lower oxygen concentration.

A mathematical model to predict y_o^m or P_{max} has not been developed at this stage, because of lack of information and experimental data, but as more information becomes available, the situation will be improved.

A new test for the minimum ignition temperature of dust clouds needs to be developed.

NOMENCLATURE

ΔH_C (net)	= net molar heat of combustion (kcal/gmole)
ΔH_{cv}	= maximum heat release (kcal/litre)
M	= molecular weight of the dust
P_{max}	= maximum explosion pressure (lb/in ²)
P_O	= explosion pressure at a particular oxygen concentration (lb/in ²)
P_{21}	= explosion pressures in air (lb/in ²)
$\left(\frac{dp}{dt}\right)_{max}$	= maximum rate of pressure rise (lb/in ² s)
$\left(\frac{dp}{dt}\right)_O^m$	= rate of pressure rise at a particular oxygen concentration (lb/in ² s)
$\left(\frac{dp}{dt}\right)_{21}^m$	= rate of pressure rise in air (lb/in ² s)
t_r	= reaction time (ms)
T_i^m	= minimum ignition temperature (°C)
x_o^m	= actual dust concentration in air (g/l)
x_2	= stoichiometric dust concentration in air (g/l)
y_O	= particular oxygen concentration (%)
y_{21}	= oxygen concentration in air (%)
y_O^m	= maximum oxygen concentration to prevent explosion (%)

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CONVERSION TABLE

1 kcal/gmole	≡	4186.8	kJ/kmol
1 kcal/litre	≡	4186.8	kJ/m ³
1 kcal/s	≡	4186.8	kJ/m ³ s
1 lb/in ²	≡	6896.6	N/m ²
1 lb/in ² s	≡	6896.6	N/m ² s
1 g/l	≡	1	kg/m ³

Table 3
Explosibility Parameters of Dusts Studied

Material	Formula	M	$y_{O_2}^m$ %	Dust Concentration		T_I^m °C	P_{max} lb/in ²	$\frac{dP}{dt}$ max lb/in ² s	t_I ms	ΔH_C nett kcal/ gmole	ΔH_{cv} kcal/l	$X_{O_2}^m$ $\frac{M t_r}{M t_r}$ kcal l s
				actual x^m g/l	Stoichio- metric x_2^m g/l							
Tartaric Acid	$C_4H_6O_6$	150	16.5	0.5	2.5	470	-	-	-	244	4.07	-
Citric Acid	$C_6H_8O_7$	192	14.0	2.0	1.77	540	43.5	358	121.5	432	3.98	36.9
Glutaric Acid	$C_5H_8O_4$	132	13.5	1.0	1.10	540	82	1200	68.3	473	3.94	52.7
Glutamic Acid	$C_5H_9O_4N$	147	13.0	1.5	1.17	500	36	281	128.1	495	3.94	39.5
Sucrose	$C_{12}H_{22}O_{11}$	342	12.5	2.0	1.19	440	87	1308	66.5	1232	4.29	108
Diphenylol Propane	$C_{15}H_{16}O_2$	228	12.0	1.0	0.53	550	83	10500	7.9	1785	4.15	991
Benzoic Acid	$C_7H_6O_2$	122	8.5	0.1	0.68	630	99	10000	9.9	740	4.12	61.3
ABS co-polymer	$C_{20}H_{23}N$	277	8.0	2.0	0.45	460	87.5	2000	43.8	2640	4.29	156
Naphthalene	$C_{10}H_8$	128	8.0	0.5	0.44	610	85.5	8500	10.1	1190	4.09	460

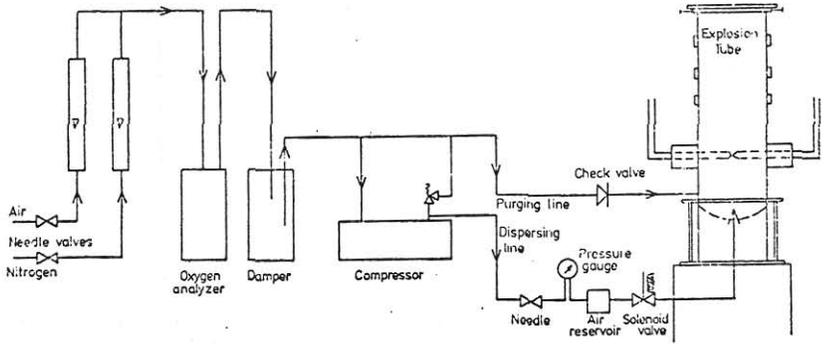


Figure 1 - Modified version of the small vertical tube apparatus.

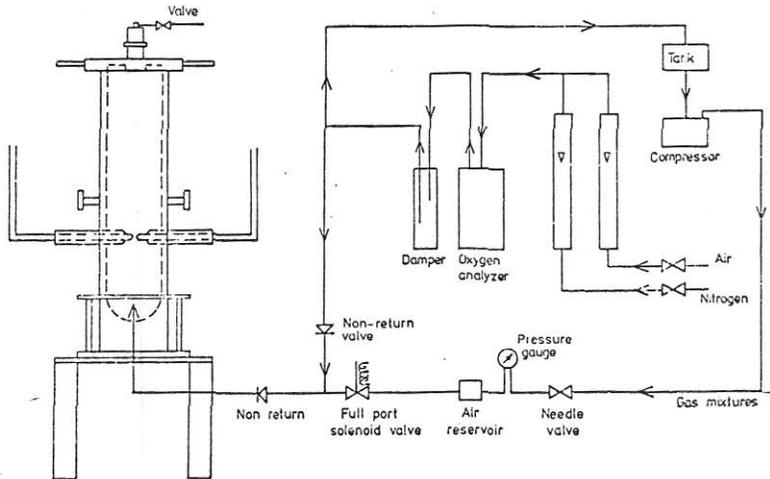


Figure 2 - Modified version of the Hartmann bomb.

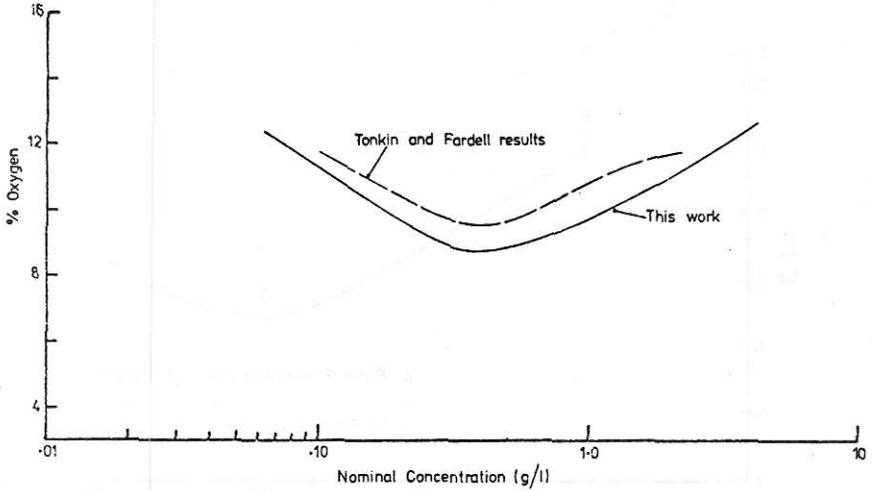


Figure 3 - Comparison between Tonkin and Fardell results and this work for the explosibility of diphenylol propane.

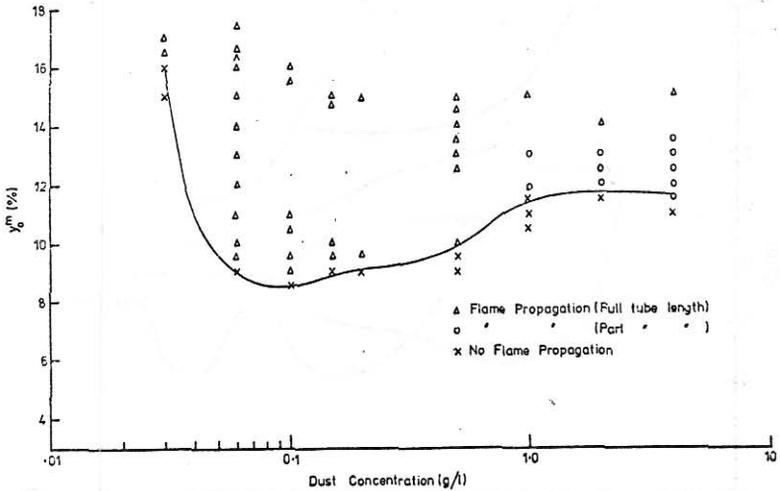


Figure 4 - The variation of y_o^m % with dust concentration of benzoic acid (g/l).

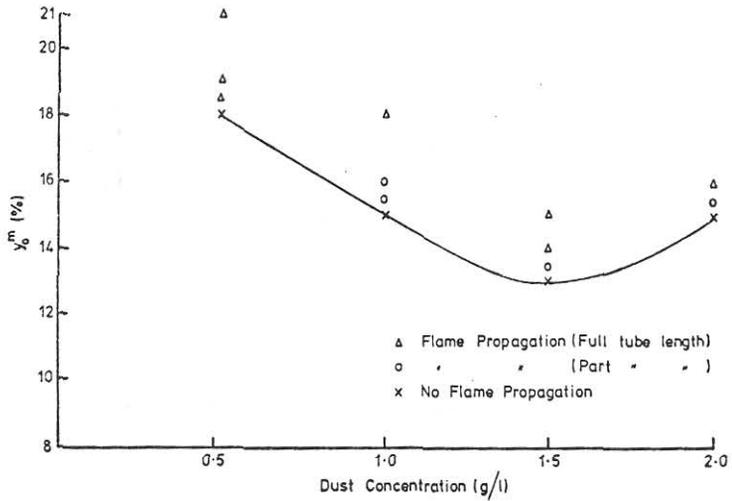


Figure 5 - The variation of y_0^m % with dust concentration of glutamic acid (g/l).

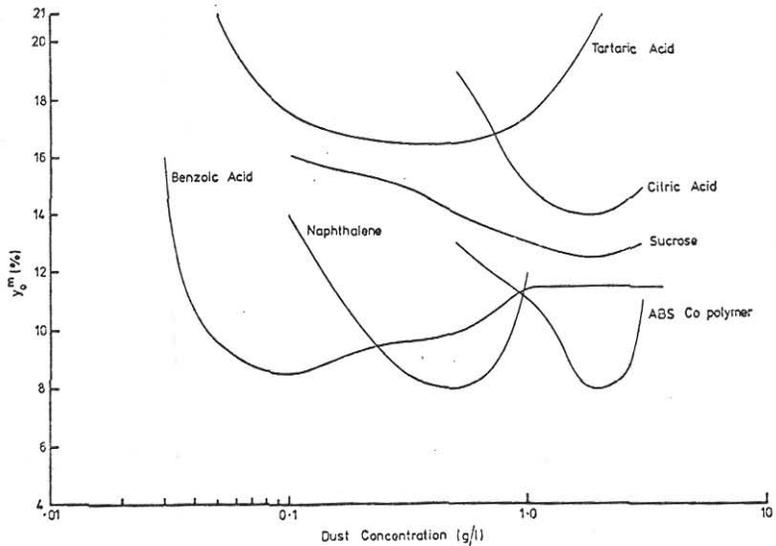


Figure 6 - Summary graphs for the variation of y_0^m % with dust concentration (g/l).

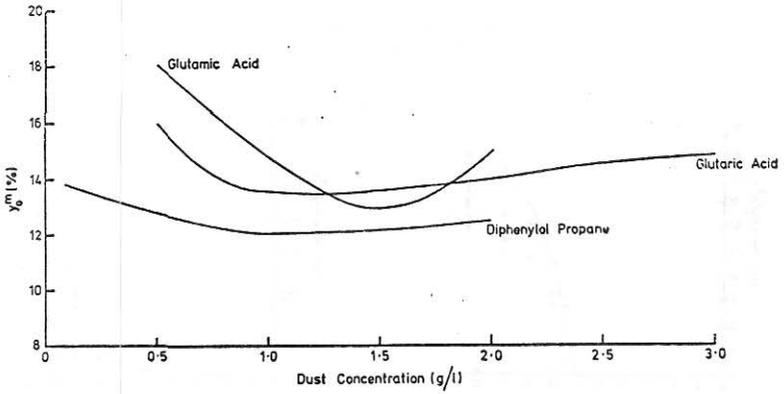


Figure 7 - Summary graphs for the variation of y_O^m % with dust concentration g/l.

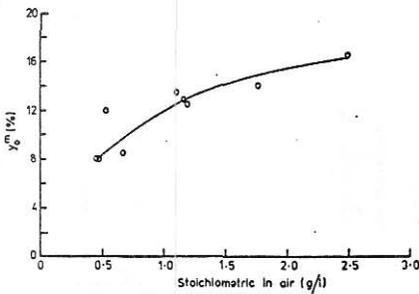


Figure 8 - The variation of y_O^m % with the stoichiometric dust concentration in air (g/l).

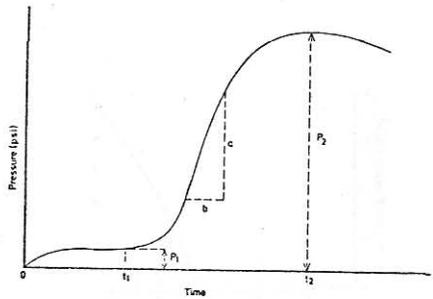


Figure 9 - A standard curve for the variation of pressure with time for any dust.

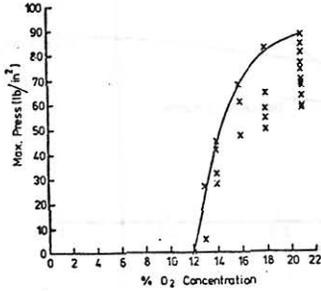


Figure 10 - The variation of P_{\max} with oxygen concentration for benzoic acid.

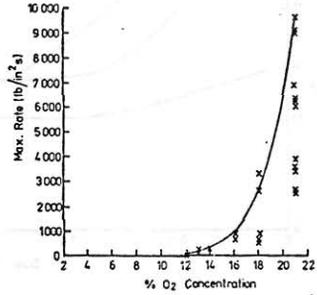


Figure 11 - The variation of $\left(\frac{dP}{dt}\right)_{\max}$ with oxygen concentration for benzoic acid.

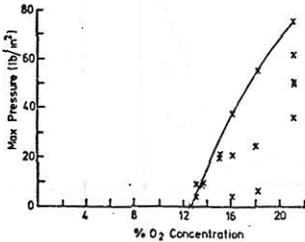


Figure 12 - The variation of P_{\max} with oxygen concentration for sucrose.

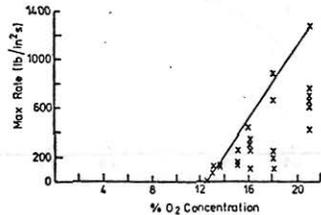


Figure 13 - The variation of $\left(\frac{dP}{dt}\right)_{\max}$ with oxygen concentration for sucrose.

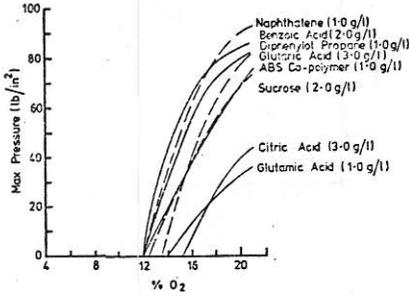


Figure 14 - Summary graphs for the variation of P_{max} with oxygen concentration.

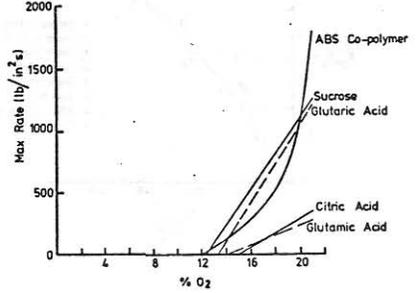


Figure 15 - Summary graphs for the variation of $\left(\frac{dP}{dt}\right)_{max}$ with oxygen concentration.

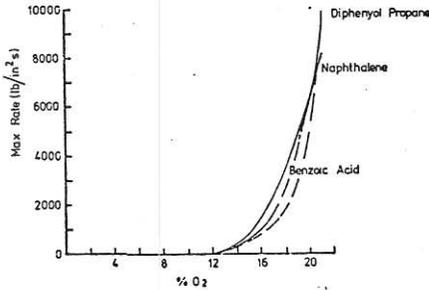


Figure 16 - Summary graphs for the variation of $\left(\frac{dP}{dt}\right)_{max}$ with oxygen concentration.

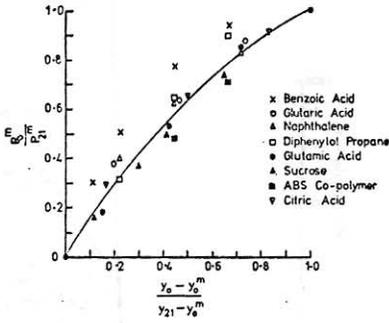
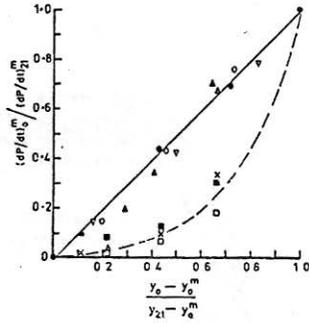


Figure 17 -
Normalised P_{\max} versus normalised
oxygen concentration.



Normalised Plots

Figure 18 -
Normalised $\left(\frac{dp}{dt}\right)_{\max}$ versus
normalised oxygen concentration.