

A NOTE ON THE LOWER EXPLOSIBILITY LIMIT OF ORGANIC DUSTS

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Summary

Measurements of the lower explosibility limits (LELs) of some organic dusts are compared to estimated values obtained by assuming that limit mixtures have a constant heat output equal to that of limit mixtures of gases and vapours. The comparison indicates that in most cases the measured LEL is a reasonable approximation to the calculated value.

1. Introduction

The general definition of the lower explosibility limit (LEL) of an explosible substance, whether it be gas, vapour or dust, is the lowest concentration of the fuel in air which will maintain a propagating flame. There are several methods for measuring dust LELs, but they are complicated by subjective judgements as to what qualifies as a limit flame and how far it should distance itself from the ignition source before it can truly be said to be self-propagating.

At a recent symposium some discussion took place on the reliability of LEL results from the various standard methods [1]. Mitcheson and Craven [2] pointed out that measurements obtained at Fire Research Station (FRS), Great Britain, using the vertical tube apparatus (described in Ref. [3]) often gave much lower concentrations than obtained in either the Hartmann bomb as used in the U.S.A. or the 1 m³ vessel (described in Ref. [4]). The authors attributed the differences to the different techniques used to specify a limit flame. At the Fire Research Station flames around the ignition source are taken to represent a limit flame, whereas, in the U.S.A., flame must fill the vessel and generate an appreciable explosion pressure. Palmer [5] responded that low values of dust/air LELs should not be discounted because the concentration at the flame front need not be the same as the nominal concentration of the dust. For their part, Mitcheson and Craven [2] suggested that the 1 m³ results could be in error because dust could remain in the injection system.

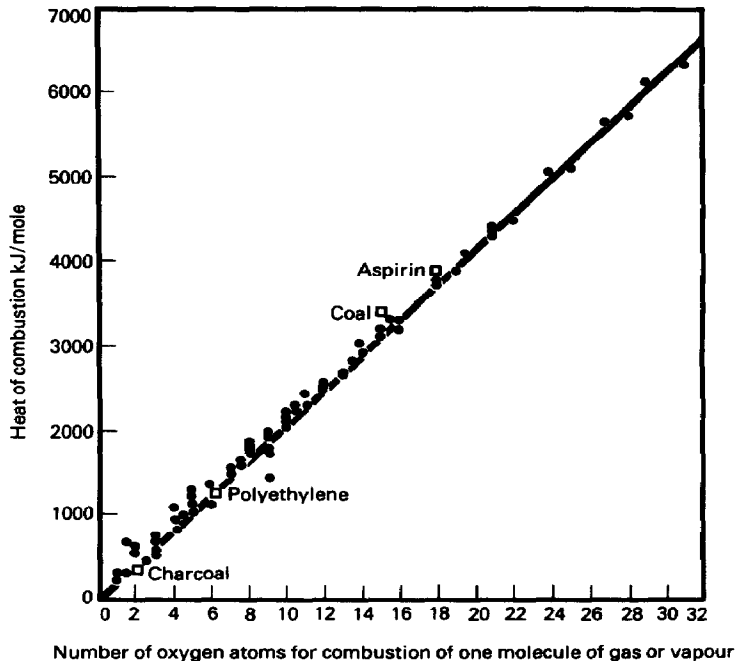


Fig. 1. Relation between heat of combustion and number of oxygen atoms for complete combustion of gases and vapours.

They noted, however, that measurements from the 1 m³ vessel are similar to limit concentration estimates based on flame-temperature considerations.

The problems associated with an ideal determination of LELs and the complications such as non-uniform concentrations that arise in practice are not easily resolved. However, in this paper, some limit concentrations for dust explosions are estimated from a comparison with the LELs of gases and vapours. These estimates are compared with experimental determinations from several sources, and some conclusions about the reliability of test data drawn.

2. Method for LEL estimations

The LEL's of most organic substances can be estimated if it is assumed that the enthalpy content of a limit mixture is constant. This is the basis of the flame-temperature method mentioned by Mitcheson and Craven. If the heat of combustion of the substance is known, then the limit concentration can be estimated. Heat of combustion data for ninety-three organic gases and vapours, listed in Ref. [6], are plotted in Fig. 1 against the number of oxygen atoms required to burn one molecule of the gas or vapour completely. The number of oxygen atoms for combustion is calculated using:

TABLE 1

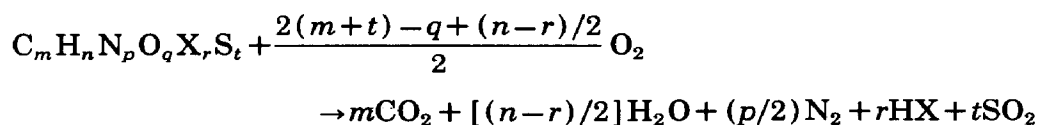
Properties of four explosible dusts

Dust	Equivalent 'molecular formula'	No. of oxygen atoms for combustion per 'molecule'	Heat of combustion* (kJ)
Aspirin	C ₉ H ₈ O ₄	18	3880
Charcoal ^b	C	2	380
Coal ^c	C _{6.6} H _{5.1} N _{0.1} O _{0.62}	15	3380
Polyethylene	C ₂ H ₄	6	1280

*Bomb calorimeter measurements.

^bAssumed to consist of carbon only.

^cComposition obtained by ultimate analysis.



where X = halogen.

Figure 1 demonstrates that, to close approximation, the heat of combustion per mole of gas or vapour is a function of the number of oxygen atoms required for combustion. Data for four dusts have been added to Fig. 1 to demonstrate that it is applicable to organic dusts. The information on these dusts is given in Table 1.

In Fig. 2, the heat output from a 1 m³ volume of the gas or vapour LEL mixture is plotted against the oxygen atom number. Most of the points fall in the range 1500–2250 kJ. Those substances falling well outside this range are either non-hydrocarbons such as COS, CS₂, C₂N₂, H₂S and H₂, or are halogenated compounds in which the halogen atoms interfere with the H/C/O combustion mechanism and so negate the thermal assumptions on which this limit theory rests, although ethyl chloride, with a heat output of 1989 kJ/m³ at the LEL, falls within the range. Generally, there is a reasonably constant value of heat output in the LEL mixtures. The scatter of points results from the structure of the molecules (type of bonds etc) and experimental uncertainty in the LEL measurements.

This result can be used to estimate the LEL of a dust-air mixture. From the composition of the dust, the mass of oxygen required for combustion of unit mass of dust can be calculated. The calorific value of this mass of dust can be obtained using Fig. 1, and the mass of dust per unit volume necessary to provide the heat output of a limit mixture (Fig. 2) calculated.

In Table 2, LEL estimates for various dusts are compared with experimental values. The LEL estimate is given as a range of concentrations to take into

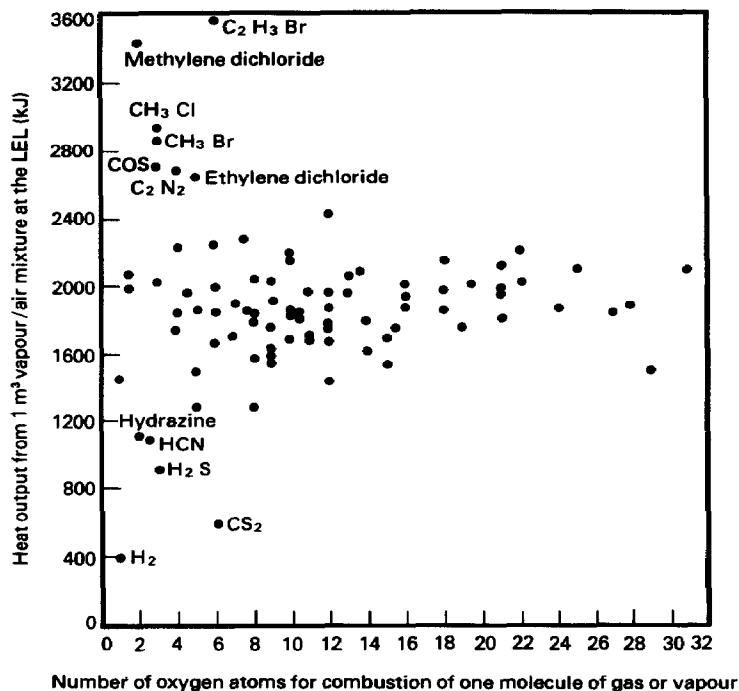


Fig. 2. Heat output from 1 m³ volume of vapour/air limit mixtures.

account the scatter of the data in Fig. 2. The experimental data from Ref. [3] have been obtained either at FRS or the U.S. Bureau of Mines (USBM) using a vertical tube apparatus. The LEL is obtained by dividing the smallest quantity of dust giving an explosion by the volume of the vessel in which the explosion occurred. The experimental data from Ref. [4] have been obtained in a 1 m³ apparatus. In this method, the tests are begun with a dust concentration of 500 g/m³. The dust concentration is reduced to 250 g/m³, 125 g/m³, 60 g/m³, 30 g/m³ and 15 g/m³. This reduction continues until, at one of these concentrations, three tests fail to yield an ignition under the standard conditions of a 10 kJ chemical ignitor and a 0.6 s delay. If, at this same concentration, no ignition occurs in three tests when the delay is shortened to 0.3 s, this concentration is defined as the LEL. It should be noted that the results from the vertical tube give the LEL as the concentration at which flame will just propagate, while the values obtained in the 1 m³ vessel are concentrations at which flame fails to propagate and should be somewhat lower than the actual values because of the discrete steps in the concentrations. Data from the 1 m³ vessel are thus presented as a range of concentrations in Table 2, and when several values of LEL for a specific dust are given, the lowest value has been taken. Reference [4] contains also some data estimated from tests in a modified Hartmann apparatus and some of this data are included in Table 2.

TABLE 2

Comparison between estimated and measured LELs of explosible dusts

Dust	Heat of combustion kJ/g	Estimated LELs g/m ³	Measured LEL 1 m ³ vessel [4]	Measured LEL Hartmann [4]	Measured LEL USBM [3]	Measured LEL Fire Research Station [3]
Acetoacetic acid anilide	27.4	55-82	30-60		30	
Acetylsalicylic acid	20.56	73-109		30		15
Acryloamide	23.38	65-96		100	40	
Adipic acid	19.17	79-117	60-125		35	
Anthranilic acid	23.70	66-99				30
Anthraquinone	29.71	50-76	30-60			
Ascorbic acid	11.80	126-191	60-125			
Calcium acetate	9.49	158-237	250-500			
Cellulose	15.34	98-148	30-60		45	
Cellulose acetate	13.14	114-173		100	35	
Cellulose acetate propionate	19.35	80-120		30		
N-cetyl-NNN tri-methyl ammonium bromide	33.2	45-67	30-60			
Charcoal	35.0	43-64	60-125		140	
Coal (37% V.M.)	19.50	77-115	60-125		55	
Cyanoacrylic acid methyl ester	19.82	76-113	30-60			
Ethoxybenzamide	26.62	56-84		100		
Hexamethylenetetramine	26.43	57-85	30-60		15	
Lactose	14.62	104-156	125-250	100		300 (crystalline)
Mandelic acid	23.03	66-99		30		
D-Mannitol	14.72	102-153	60-125		65	
Melamine	15.25	102-152		1000		
Methacrylic acid amide	25.64	58-88	15-30			
p-Nitroaniline	19.49	77-115	30-60			
Paraformaldehyde	14.0	107-161	60-125		40	
Pentaerythritol	18.38	82-122	30-60		30	
Phenylbutazone	38.3	39-58		100		
Phenylenediamine	30.56	49-74		30	25	
Phthalic anhydride	20.94	72-107		100	15	
Polyacrylate	21.62	69-104	30-60			
Polyacrylonitrile	30.18	50-75	15-30		25	
Polyethylene	44.64	34-50	15-30	30		10
Polymethacrylate	24.80	60-91	30-60			
Polypropylene	44.29	34-51	15-30	30	20	
Polystyrene	31.70	38-57	400 (650 μ m)	30	20	
Polyurethane	15.28	96-144	30-60	100		40
Polyvinyl acetate	21.62	69-104	60-125		40	
Polyvinyl alcohol	23.63	63-95	15-30			
Polyvinyl butyral	21.38	52-78	30-60	20		
Polyvinyl chloride	16.13	90-150		30		
Salicylic acid	21.67	70-105	60-125	30	25	
Starch	15.31	98-147				

This method does not pinpoint dusts that, although fulfilling the requirements of a combustible dust, are not in practice capable of propagating flame when dispersed in air. This can arise because volatiles may either not be sufficient or not be released rapidly enough to sustain a flame. In other circumstances the particle size may be too large to propagate the explosion (wood and paper fibres, polyethylene shreds, for example), and the water content may be high [4]. The dust may also contain elements which can interfere with the combustion process, for example, polyvinyl chloride. Some indication that these dusts may not easily propagate flame can be obtained from Fig. 2, which shows that, generally, limit mixtures of halogenated compounds contain a larger concentration of the compound than do limit mixtures of similar unhalogenated compounds. Nevertheless, as Ref. [4] shows, when the particle size of polyvinyl chloride is low ($< 10 \mu\text{m}$) it is capable of propagating an explosion and generating an explosion pressure of about 9 bar. These remarks show that, in practice, there is no substitute for a lower explosibility limit measured by an accepted method. The present arguments are put forward simply to suggest that these measurements can be accepted as giving reasonably realistic values of the LEL.

Conclusions

The comparisons given in Table 2 essentially confirm the conclusions of Mitcheson and Craven [2]. Apart from one or two examples, the data from 1 m^3 vessel tests give LEL values that are below the estimated concentrations. There is an in-built safety factor with these results that can sometimes be substantial. Calcium acetate and polystyrene are examples of the substances where the measured LEL in the 1 m^3 vessel is higher than the estimated value. In the case of polystyrene this may be due to the large particle size ($650 \mu\text{m}$), but there are other examples in Table 2 where a large particle size has not meant a high measured LEL.

The measurements in a Hartmann apparatus given in Ref. [4] are estimates only and are limited to 20, 30 or 100 g/cm^3 . These values should not be relied on.

The experimental data from the USBM and FRS tests generally give reliable values of the LEL, of the same order as obtained in the 1 m^3 vessel. The USBM measurement of the LEL of polystyrene is more in keeping with the estimated LEL than is the 1 m^3 vessel measurement.

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