

AUTOIGNITION TEMPERATURE DETERMINATIONS & THEIR RELATIONSHIP TO OTHER TYPES OF  
POTENTIAL IGNITION SOURCES & THEIR APPLICATION TO PRACTICAL SITUATIONS

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Developments in the measurement of autoignition temperature values are reviewed and the differences between various methods noted. For certain applications, the volume of mixture which can potentially ignite is considerably different to that used in laboratory determinations and the effect of volume on autoignition temperature is analysed. A method of extrapolation which links in to data relating to flame kernel establishment by other ignition sources is outlined and the application of autoignition temperature values to practical situations is discussed in detail.

INTRODUCTION

Standard test methods for the determination of autoignition temperatures of vaporised liquids and gases in air at atmospheric pressure have been available in various forms since 1930. A considerable number of values for different fuels (both as pure materials and mixtures) have been published and have found specific application as regards the selection of electrical equipment for hazardous locations.

Recently there have been developments relating to new methods for determining a reaction threshold temperature for liquid and solid materials in air and also regarding the distinction between the temperatures at which cool flame behaviour will be produced and at which normal combustion type flames result.

The combination of economic pressures and higher standards of chemical processing safety is leading to the increasing use of autoignition temperature values under conditions widely different from those used to determine them.

As a result it is appropriate to review the autoignition temperature test methods and techniques for the application of such values to practical situations.

ESTABLISHED AND NEW AUTOIGNITION  
TEMPERATURE DETERMINATION METHODS

ASTM proposed a test method in 1928 in which a conical flask of pyrex glass was heated in a solder bath. This method became ASTM Standard D286 (1) in 1930 and remained as a definitive standard until 1958. Thompson (2) published the results of work carried out at Factory Mutual in which autoignition temperature

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determinations inside round and conical flasks were compared with results obtained in machined copper, low carbon steel and chromium plated steel recesses in blocks of metal 10.2 cm in diameter by 11.4 cm long. Thompson (2) concluded that Pyrex glass flasks were preferable to machined metal apparatus when used to test 37 different liquids.

This method of test using a nominal 125 ml conical flask was replaced by a commercial 200 ml Erlenmeyer pyrex flask in a special electrical furnace with a bottom heater, cylindrical heater and a top neck heater which could be individually controlled so that three thermocouples in contact with the outside of the flask are within 2°F (1.1°C) of the desired test temperature in 1963. This method was accepted internationally as ASTM standard D2155 (3), German standard DIN 51794 (4), British Standard 4056 (5) and by the International Electrotechnical Commission (6). These standards show slight variations between each other as regards the procedures adopted but the apparatus used is substantially the same. These standards are regularly reviewed and updated and it is noteworthy that (5) and (6) contain procedures for the injection of gaseous fuels as well as liquid fuels.

Recently, ASTM have issued a new test method D 2883-72 (7) for liquid and solid materials which uses a 1 litre stainless steel spherical reaction vessel which is located within a heated oven and can be used to study the onset of a reaction, a cool flame propagation or a hot flame reaction at predetermined temperatures and pressures up to 650°C and from a low vacuum up to 0.8 MN/m<sup>2</sup> pressure. In this test method, the sample is sealed within a glass ampoule at the start of each experiment and arrangements are provided for the ampoule to be broken when desired. The behaviour of each experiment is observed by means of a bare junction thermocouple inside the reaction vessel and a temperature recorder.

#### DATA ON AUTOIGNITION TEMPERATURES OF FUELS

A number of reviews of autoignition temperature values have been made at various times and some of these are regularly updated as part of compilations of hazard data for flammable materials. Two reviews where the results using different materials for the test vessel are compared are those of Matson & Dufour (8) and Riddlestone (9). These conclude that glass or quartz vessels are generally found to give the lowest autoignition values. Other materials are concluded to give rise to wall reactions and catalytic effects and also that the maintenance of an "as new" surface condition is more difficult with metallic materials due to surface oxidation and pitting compared with glass and quartz (quartz used for temperatures above the softening point of borosilicate glass).

The standard sources of values for autoignition temperature values are:-

- (i) International Electrotechnical Commission First Supplement to Publication 79-4 (10).
- (ii) British Standard Code of Practice BS5345 Part 1 (11).
- (iii) The German listing of flammable material properties by Nabert & Schön (12).
- (iv) US Bureau of Mines Bulletin 627 (13).
- (v) The Fire Protection Association tabulation of 1974 (14).

- (vi) The ICI Electrical Installations Code published by RoSPA (15).
- (vii) The NFPA listing of Fire Hazard Properties (16).

These tabulations are found to give the same values for most fuels and the data listed have been determined at atmospheric pressure by one of the standard 200 ml Erlenmeyer flask methods (3), (4), (5) and (6).

For each fuel (normally tested as a material of standard purity grade or as a controlled product when a mixture is concerned), a single temperature is quoted. This represents the minimum temperature at which flame was observed within the test period of 5 minutes and the accuracy of the method is of the order of  $\pm 2\%$  to  $\pm 3\%$  of the actual degrees Celsius value determined.

#### THE MEANING OF THE STANDARD AUTOIGNITION TEMPERATURE VALUE

The establishment of an autoignition temperature value for a given fuel requires the carrying out of a considerable number of repeat tests with variations of the flask temperature and the amount of fuel injected. Various methods of injecting the fuel are discussed by Riddlestone (9) and the standard methods only call for "the sample to be injected as quickly as possible, so that the operation is always completed in 2 seconds". The conditions which are involved in the physical injection of fractions of a ml of liquid are quite different to those when 50 to 100 ml of a gaseous fuel has to be injected. The inevitable result is that it is impossible to standardise the addition rate of the fuel.

The result of the fuel addition process is that a complex interaction of fuel heating (and for liquids the vaporisation of the fuel) with fuel-air mixing takes place and the pattern of air movements within the flask tends to be highly variable. The flask contents will be non-uniform in fuel distribution over the flask volume and show varying amounts of convection and eddy motion at the time that ignition takes place. Consequently, little significance can be attached to the variations in autoignition temperature found as the quantity of a given fuel is injected. The experimental boundary between ignition and non-ignition conditions will be generally as shown in Figure 1, but odd results of non-ignition behaviour can be observed above the boundary line especially when the amount of fuel injected is not the optimum quantity (as shown on Figure 1).

The actual volumetric capacity to the top of a 200 ml Erlenmeyer flask of standard design will vary due to the customary allowances for glass articles. These are found to range from 225 ml to 305 ml when a number of pyrex and quartz flasks are measured. For the case of propane in air (shown in Figure 1), the recognised optimum concentration of propane for combustion is between 4.5 and 4.8% v/v. The lower limit at room temperature is 2.1% v/v and from Zabetakis (13) (using the modified Burgess-Wheeler Law) this can be corrected to 550°C to give a value of 1.2% v/v propane. Now if the optimum quantity of 80 ml of propane corresponds to say 4.8% v/v propane, the lower limit at 550°C (on a proportional basis) would correspond to 20 ml of propane. The curve of autoignition temperature variation with fuel quantity injected shown on Figure 1 does not show as rapid an increase of autoignition temperature over the range 40 to 30 ml of propane as would be expected if 20 ml of fuel corresponded to a limit mixture at 550°C. Such behaviour is what would be anticipated if the mixture in the flask was non-uniform in composition.

(13) can also be used to estimate the upper flammability limit of propane in air at 550°C. This calculation will tend to underestimate the true value as cool and decomposition flame behaviour will not be adequately estimated. The value so calculated is 13.1% v/v for propane in air.

In Figure 1, the quantity of 80 ml propane appears to correspond to the optimum mixture expected to be 4.8% v/v propane. An average total flask volume of 250 ml would lead one to expect 80 ml propane to give at least 20% v/v of fuel in the flask. To assess the problem of average composition, some experiments were carried out by injecting anhydrous ammonia in varying amounts into a flask at room temperature using the normal fuel injection method. At the end of the injection period, the top of the flask was covered and the average amount of ammonia remaining in the flask evaluated by absorption in water and titration with N/10 HCl using Methyl Red as an indicator. The results obtained for two different flask volumes are given as Figure 2 which shows that the injection process is progressively wasteful as regards fuel retention in the flask as the volume injected is increased. The use of these curves to "calibrate" test results such as Figure 1 is not justifiable as different conditions will apply in a hot flask due to the expansion of a gaseous fuel or vaporisation of a liquid fuel at different flask temperatures.

Experiments can be carried out to establish a specific autoignition temperature for a given fuel-air mixture composition but using a more involved technique. Complex apparatus such as is shown in Figure 3 is necessary to prepare the fuel-air mixture at a temperature below the value at which any reaction occurs but sufficiently high to keep the fuel as vapour and then allowing it to quickly fill a heated and evacuated ignition experiment vessel. Such experiments have normally to be carried out within metallic equipment and are subject to the disadvantages of metallic surfaces compared to those of glass and quartz as discussed above.

The amount of work involved in a standard autoignition determination by the methods given in (3), (4), (5) and (6) is of the order of 30 to 40 experiments taking about 4 days to carry out for a simple system where the autoignition temperature is known approximately. For a fuel where the autoignition temperature is not known approximately and where the flammability limits are not recorded in the literature, the amount of work involved is increased by a factor of between 2 and 4.

If the alternative method of admitting premixed fuel and air to an evacuated experiment vessel is assessed for work content, about the same amount of time (4 to 10 working days) can be required to define autoignition temperature values for about 2 or 3 mixture compositions. Up to 10 different compositions need to be studied in order to define the minimum point of the autoignition curve for the fuel and this serves to illustrate the very considerable experimental effort that is required to define a composition against autoignition temperature curve for a given fuel.

As a result of this, the minimum temperature as obtained from a curve such as Figure 1 is used for a given fuel on the basis that variations in fuel concentration are to be anticipated in practice and that the test method itself has simulated releases of fuel into hot zones with the attendant mixture variations and turbulence in the potential zone for autoignition. Where conditions inside process equipment are being evaluated, the mixture may be definable and not approaching the optimum composition. Then a safety margin (perhaps of the order of 20°C or more) may exist over the standard minimum autoignition temperature for the fuel.

EFFECT OF VOLUME OF TEST VESSEL ON  
MINIMUM AUTOIGNITION TEMPERATURE VALUE

The early work on the determination of autoignition temperatures such as that of (2) considered that the result was more dependent on the material out of which the test vessel was made (and the condition thereof) than the size and shape of the vessel. For experimental reasons most tests were carried out using a test volume in the range 100 to 300 ml in capacity having physical diameter values of the order of 60 mm to 85 mm. This choice of vessel size can be defended as logical as it is of the same order as the US Bureau of Mines Flammability Apparatus (50 mm diameter) - (13) and its predecessors - and also similar to closed flash point apparatus cups which range from 49 mm to 54 mm in diameter. The "typical" autoignition apparatus dimension therefore appeared to be quite adequate for the establishment of "standard" combustion parameters.

In a general review of the subject in 1954, Setchkin (17) presented many results obtained over a period of about 15 years and confirmed many of the factors which can appreciably affect the temperature values obtained. The effect of a change in volume of a spherical vessel was studied on 19 different fuels using pyrex flasks of 8 ml, 35 ml, 200 ml, 1 litre and 12 litre volume and an opaque silica flask of 15 litre volume. The influence of vessel size was shown to be that of a reduction in ignition temperature as the size was increased when the vessels were made of the same material. The 15 litre opaque silica vessel was found to give higher temperature values than the 12 litre pyrex vessel and this was attributed to the different nature of the vessel wall. The 12 litre pyrex flask was found to be unweildy and fragile and the 1 litre size was recommended as a suitable standard unit.

These results (17) for the same fuel in the 8 ml and 12 litre flask sizes showed a reduction in temperature of at least 52°C (di ethyl ether) and a maximum reduction of 209°C in the case of acetone.

This quite startling reduction of autoignition temperature as the flask volume is increased above a standardised value (eg 200 ml Erlenmeyer flask) and the corresponding increase of autoignition temperature when the flask volume is substantially smaller than the standardised value has largely been ignored in the application of standard autoignition temperature values to practical situations.

The difficulty in dealing with this effect of vessel volume can be traced to the following factors:-

- i) The lack of any recognisable similarity in the volume effect with different fuels.
- ii) The accuracy of established methods is such that a given operator following the technique cannot produce results more accurate than to  $\pm 1\%$  of the actual °C temperature. This has to be compared with the observed reduction of from 6% to 25% of the actual °C temperature value by a volume increase from 200 ml to 12 litres.
- iii) The lack of a basis for relating flask volumes of different shapes to each other.
- iv) The observations made with the larger vessel sizes tend to show different behavioural patterns to those in quite small vessels (flameless reaction and cool flame effects are observed as well as

normal combustion flames).

- v) How the effects of ignition delay should be assessed in using determinations made in different sizes of vessels.
- vi) The physical difficulties introduced by the injection of the larger fuel quantities in comparable times in using large test vessels (especially with flammable gases).
- vii) Different characteristics presented by the relative neck of a flask as regards breathing and fuel losses with different flask volumes as dimensional similarity is not maintained in commercial flask designs of different capacities.

Recently, both Coffee and D'Onofrio of Eastman Kodak have published results showing the effect of volume change of the test vessel on the autoignition temperature with the heating arrangements and test method remaining unvaried (18) and (19). In the first case (18), the effect of increasing the size of a conical Erlenmeyer flask from 200 ml nominal to 500 ml nominal for 6 materials and in (19) different spherical flask were used in an oven. The size range tested in (19) was from 218 ml up to 5.4 litre and concerned 4 different glycols. These investigations were concerned with the reproducible appearance of cool flames as a result of autoignition phenomena at temperatures considerably lower than the temperatures at which normal flame autoignitions occurred. Other work by Beerbower of Exxon (20) which was reported to ASTM Committee D-2 is referred to in these papers from Eastman Kodak.

Other work relating to the effect of vessel size has been carried out by workers at RAE Farnborough (21) for studies on Avtur kerosine fuel and (22) for M86 hydrazine type fuel. The RAE work was carried out using stainless steel vessels ranging in diameter from 25 mm up to 0.46 metres in diameter. The Eastman Kodak work (18) and (19) was carried out inside pyrex flasks as was some work on 2,2-Dimethyl Butane carried out at the Naval Research Laboratory (23).

It is clear from an examination of all these results relating to the influence of vessel volume that the reduction in the autoignition temperature as the vessel size is increased is always observed whilst a similar flask material and surface condition is used. The trend in temperature reduction with increasing size can be accelerated in larger vessels if cool flames are used as an indication of autoignition or alternatively if a sensitive thermocouple is used in the flask. This technique is frequently used with closed metal vessels where visual observation is not possible. Fine, Gray & MacKinven (24) have shown under sub-atmospheric conditions in a 1.2 litre spherical vessel that a slow reaction can with some materials be observed under a slightly lower temperature than the value at which a cool flame will be observed. Similar results have been observed in studies of a number of other materials and the ASTM method D2883 (7) is specifically written to allow for the determination of the temperature at which such a slow reaction will be initiated.

Most of the data for normal auto-ignition temperature variations with vessel volume relate to spherical vessels having radii between 12.4 mm and 230 mm. This variation in spherical volumes is however small compared to the conditions of application of autoignition temperature values which can vary from a few mm in dimension up to volumes of tens of metres in diameter or more. A basis of extrapolating the known experimental variations is therefore

required plus the comparison between different shapes of a containing vessel of specified volume.

#### AUTOIGNITION TEMPERATURE - VOLUME RELATIONSHIPS

A number of relationships have been proposed in (18), (19) and (22) for the extrapolation of autoignition temperature values. The relative small range of test vessel radii and the inherent experimental inaccuracies of the determinations allow many of these relationships to be shown to fit approximately.

The use of larger vessel radii for experimental verification of a scale relationship is not practical due to the considerable experimental difficulties involved. Also the advent of cool flame and slow reaction effects on a more significant scale presents severe interpretation difficulties in such work.

As a result, the interaction of autoignition behaviour with other methods of ignition and critical flame propagation has been considered. As the test volume is made progressively smaller, it must approach the critical condition of a flame kernel which is just capable of initiating an expanding flame front. Data relating to flame kernel sizes can be obtained from electrical ignition energy minimal values, quenching diameter measurements and limiting flame temperature values.

Careful examination of a number of autoignition temperature values in different spherical volumes can be used to verify the validity of various relationships using the flame kernel size and lower limit flame temperature value as a reference point. This has been carried out and the following statements summarise a satisfactory extrapolation method which is based on a number of scientific treatments.

Differences in shape of test vessels can be related to a spherical shape for volume relationship calculations by means of the Semenov equivalent sphere radius concept of Boddington, Gray and Harvey (25). This radius  $R_0$  is defined as the harmonic square mean radius weighted in proportion to solid angle and is calculated by the relationship

$$\frac{1}{R_0^2} = \frac{1}{4\pi} \int \frac{d\omega}{r^2} \quad (1)$$

where  $\omega$  is solid angle and  $d\omega = \sin\theta d\theta d\phi$  for a surface defined using spherical polar co-ordinates  $r = F(\theta, \phi)$  in the usual system  $r, \theta, \phi$ .

Using this, the Semenov equivalent radius for a 200 ml Erlenmeyer conical flask has been calculated as 34 mm for normal pyrex versions and 38 mm for some quartz versions we have had made which turned out to be slightly larger (about 290 ml total volume).

The extrapolation of the autoignition temperature value  $T_0$  (in  $^{\circ}\text{K}$ ) is then made by plotting  $\ell_n \frac{T_0^2}{R_0}$  against  $\frac{1}{T_0 - 288}$ . This gives a straight line plot as these terms can be shown to be related in the following manner:-

$$\ell_n \frac{T_0^2}{R_0} + A = - \frac{B}{T_0 - 288} \quad (2)$$

This is slightly different to the relationship given in (22) but can be shown to be consistent with the treatment in (25). The value for ambient temperature  $T_a$  in (25) has been taken as  $288^{\circ}\text{K}$  (the basis of the standard atmosphere conditions).

The detailed discussion of this relationship is being reported elsewhere with the differences between this and the various other autoignition temperature - volume relationship referred to. Based on the data obtained from the published experimental autoignition - volume investigations plus some work carried out at Mond Division Explosion Hazards Laboratory on n-Butane, Propane and Cyclohexane in flask sizes from 25 ml Erlenmeyer up to 5 litre spherical, satisfactory straight line relationships have been obtained for a total of 15 fuels in air as a verification of equation (2).

The results of this analysis of the experimental data is presented in Table I for the 15 fuels. The standard 200 ml Erlenmeyer flask value is quoted plus values derived from the extrapolation method for a spherical volume of radius 10 mm and large spherical volumes of radius 1 metre and 2 metres. The standard 200 ml Erlenmeyer flask value in a few cases is between  $5^{\circ}$  and  $10^{\circ}\text{C}$  different to the line drawn through other points such as the volume - autoignition temperature values due to Setchkin and as this is within the known accuracy value of such determinations ( $\pm 2\frac{1}{2}\%$  of the  $^{\circ}\text{C}$  value) no attempt has been made to resolve this type of discrepancy. The extrapolated values are considered to be within  $\pm 2\frac{1}{2}\%$  for the 10 mm radius extrapolation and probably within a band ranging from the 1.03 times the value given to 0.60 times the value given for the 1 metre and 2 metre radius extrapolations. This larger band on the lower temperature side is specified to take account of the cool flame autoignitions reported by Coffee and D'Onofrio (18) and (19).

TABLE I - Effect of Different Volumes on the Autoignition Temperatures in Air at Atmospheric Pressure

Fuel	Standard AIT $^{\circ}\text{C}$ in 200 ml Erlenmeyer Flask	Extrapolated AIT $^{\circ}\text{C}$ Value for		
		Spherical Volume of 10 mm Radius	Spherical Volume of 1 metre Radius	Spherical Volume of 2 metre Radius
Acetic Acid	485	619	364	342
Acetone	535	654	371	349
Benzene	560	646	410	390
n-Butane	365	514	223	207
Carbon Disulphide	102	150	74	70
Cyclohexane	259	329	170	161
Di Ethyl Ether	170	229	122	115
Ethanol	425	511	296	280
Ethylene Glycol	410	512	312	296
n-Heptane	215	285	143	133
Methanol	455	524	330	313
n-Pentane	285	339	186	176
Propane	470	563	351	332
Toluene	535	630	419	400
m-Xylene	525	623	401	381



PRACTICAL APPLICATIONS OF AUTOIGNITION  
TEMPERATURE VALUES

The application of autoignition temperature values as represented by the standard 200 ml Erlenmeyer flask values requires some careful consideration according to three factors:-

- a) The size of the practical volume being considered
- b) Whether the potentially ignitable mixture will be nominally in a quiescent state or under flow conditions
- c) Whether the mixture composition is subject to control as regards fuel proportion or not.

A number of practical situations can be identified which need consideration:-

- i) Small electrical equipment enclosures of the Intrinsic Safety category.
- ii) Relatively small pocket volumes inside or outside equipment where high local surface temperatures are present.
- iii) Medium to Large reactor volumes or pipework where heated process mixtures may have the potential to autoignite.
- iv) Large to very large volumes which may be formed by hot fuel releases into the surrounding atmosphere.

The use of autoignition temperature values for each of these broad categories will now be separately considered.

Small Electrical Equipment Enclosures of the Intrinsic Safety Category

The relevant concern in the safe design of Intrinsically Safe electrical equipment relates to the allowed maximum surface temperature of electrical items in general. Specifically, individual components such as resistors etc are recognised as permitting special consideration. Clause 4.4 of BS5501: Part 1 (26) defines small items as "components having a total surface area of not more than 10 cm<sup>2</sup>" when the normal allowed surface temperature allowed in Clause 4.1 of this standard can be exceeded. Table II summarises the situation by listing the standard autoignition temperatures (Internationally agreed values (10) being given preference to British Standard values (11)). Also given is the elevation of temperature from Table I using a 10 mm spherical volume and the Electrical Ignition Temperature Class T<sub>1</sub> to T<sub>6</sub> taken from BS5501 Part 1 (26).

The extrapolated values derived by the technique outlined above are seen to provide adequate justification for higher temperatures as given in Clause 4.4 of BS5501 Part 1. The surface volume of a 10 mm radius sphere is 12.57 cm<sup>2</sup> and therefore the comparison made in Table II is sound (in fact it is over cautious as a 10 cm<sup>2</sup> sphere would have a smaller radius of 8.9 mm).

TABLE II - Small Volume AIT Conditions

Fuel	Standard AIT in 200 ml Erlenmeyer Flask °C	Elevation of Standard AIT for 10 mm Spherical Radius Volume °C	Electrical Ignition Temperature Class and allowed Maximum Surface Temperature °C	Allowed Maximum Surface Temperature for Components not more than 10 cm <sup>2</sup> area - °C
Acetic Acid	485	134	T1 - 450	50° below small component test
Acetone	535	119	T1 - 450	50° "
Benzene	560	86	T1 - 450	50° "
n-Butane	365	149	T2 - 300	50° "
Carbon Disulphide	102	48	T5 - 100	25° "
Cyclohexane	259	70	T3 - 200	50° "
Di Ethyl Ether	170	59	T4 - 135	25° "
Ethanol	425	86	T2 - 300	50° "
Ethylene Glycol	410	102	T2 - 300	50° "
n-Heptane	215	70	T3 - 200	50° "
Methanol	455	69	T1 - 450	50° "
n-Pentane	285	54	T3 - 200	50° "
Propane	470	93	T1 - 450	50° "
Toluene	535	95	T1 - 450	50° "
m-Xylene	525	98	T1 - 450	50° "

The elevation of the ignition temperature given in Table II is plotted against the standard autoignition temperature in Figure 4 together with the classification ranges of autoignition temperatures (27). The rather unsatisfactory method in Clause 4.4 of BS5501 Part 1 of relating this allowed higher temperature to special tests involving small components is seen to be capable of improvement by extrapolation of autoignition temperatures as shown in Table II and Figure 4.

It should however be noted that data for the small volume effect on materials such as hydrogen, acetylene, ethylene oxide, ethylene, propylene oxide, propylene and other highly reactive gaseous fuels is not available at this time to complete the assessment.

#### Small Trapped Volumes Inside or Outside Equipment

This situation can be expected to arise in many different ways. A small pocket of air, vapour or gas can be externally present in a stagnant location close to a bearing or gland assembly of a pump or motor which is in need of maintenance and is running excessively hot. If the location is such that the volume is confined by hot surfaces in most directions, the volume can be expected to attain a temperature approaching that of the hot surfaces.

Clearly some fuels will have a greater tendency to show cool flame behaviour than others and it is noteworthy that all the cool flame autoignition temperature values reported relate to fuels which would be expected to give cool flames in other combustion studies - see (13). In assessing whether an allowance for possible cool flame effects on scale up it is recommended that a study of combustion behaviour should be made to identify if cool flame phenomena are likely at the specific size and pressure under consideration.

The final values in Table I corresponding to a 2 metric spherical radius autoignition condition can be used to approximately judge the effect on volumes which are different to a 1 metre radius. Various simple expressions for standard geometrical configurations for the Semenov equivalent radius  $R_0$  are to be found in (25).

#### Large to Very Large Volumes of Fuel-Air Mixtures Formed by Hot Fuel Releases to the Atmosphere

In this section, one is concerned with the autoignition potential when hot fuel is released to atmosphere when a fuel-air cloud which is flammable can be formed at an elevated temperature. Such clouds can be 10's to 100's of metres in diameter and they are frequently of the shape of an oblate spheroid when elevated above the ground (the most likely condition for autoignition). The values given in Table I corresponding to the 1 and 2 metre radius spherical volumes can be further extrapolated by the same method to larger volumes as required. It will however be found that the rate of decrease of the autoignition temperature will be progressively reduced - particularly with systems having relatively low autoignition temperature values (less than 200°C) as can be confirmed by a comparison of the 1 metre and 2 metre radius values in Table I. It can therefore be concluded that the risks of forming an aerial cloud that will autoignite will be reasonably high in the cases of carbon disulphide and di-ethyl ether if these are released at elevated temperature. The high value of the upper limit of these fuels in air allows a flammable mixture to be formed where the air dilution is not very large.

Similar results could be anticipated in the cases of ethylene and ethylene oxide. With fuels similar in character to the other 13 of Table I, the cloud will contain at least 90% v/v air in order to be flammable and the heating of large volumes of air by the fuel to temperatures significantly above 100°C would appear to be improbable.

There can however be certain conditions of semi-confinement or total confinement by a building where circumstances can combine to set up the required minimum level of air dilution plus the cloud temperature - volume relationship whereby autoignition can take place.

#### CONCLUSIONS

From this analysis of autoignition temperature values it is shown that they can be modified for use with small and large volumes by the use of an extrapolation linked to flame kernel establishment ignition requirements. The use of an additional temperature allowance in the case of the design of intrinsically safe electrical equipment is shown to be justified.

In the case of volumes of a cubic metre or more, the hot flame autoignition temperature is significantly lower than the standard value. Allowance for this in practical applications should be made plus a further allowance in the case of materials where cool flame phenomena is to be anticipated.

Providing the volume concerned is not more than about 70 mm in diameter (ie having the same Semenov equivalent radius as the 200 ml Erlenmeyer flask), the use of the standard autoignition temperature value for the limiting surface temperature can be justified as defining ignition condition. Some safety margin of about 5% of the autoignition temperature value or 20°C whichever is the largest should however be applied in such applications.

The above arguments can also apply to hot volumes that may collect around partly recessed bearing/gland assemblies in branches fitted to reaction vessels. Most of these volumes are likely to be small if they are to be expected to become appreciably hotter than the main vapour space in the vessel. The standard autoignition temperature is again recommended as the design parameter except that in this case there is usually a built-in safety factor in that the mixture composition is not likely to be near an optimum combustion one for obvious reasons. It is more likely to be on the fuel-rich side and under these conditions attention must be directed to the assessment of whether cool flame behaviour is to be anticipated. If this is the case, an allowance for a reduction in the safe temperature should be made. This can in some cases be "offset" by the raising of the autoignition temperature by the characteristics of the volume having a Semenov equivalent radius significantly below 35 mm.

However, the pressure inside a reaction vessel can be significantly different from atmospheric. Increasing the system pressure is known to have an effect of reducing the autoignition temperature value (18), (27) and (28). The formulation of general rules for the effect of pressure is not possible due to lack of experimental data, the tendency for cool flame phenomena to be more important at higher pressures and variations in the test apparatus and method between atmospheric and elevated pressures. Literature on cool flames largely deals with cool flame behaviour under partial vacuum conditions where hazards are created as a result of air leakages into a system containing fuel. An adequate temperature safety margin is recommended where such applications have to be rendered safe by temperature considerations.

#### Autoignition Inside Medium to Large Process Volumes or Pipework

This application needs to be considered on a similar basis to potential autoignitions of small heated and trapped volumes inside equipment but with the addition of two factors. The first is the effect of increasing the volume involved which, as reference to Table I for a 1 metre radius spherical volume shows, can result in a significant lowering of the autoignition temperature. The second is that such larger volumes can be in a well agitated or flow condition which has been shown to raise the general requirements for ignition due to the disturbance by movement of the initial phase of reaction which could result in the establishment of a propagating flame kernel under static conditions. Other work relating to the rapid flow of gas mixtures has shown a tendency for autoignition to occur at lower temperatures than expected due to aerodynamic friction effects, ionisation of a gas mixture constituent or transient temperature changes associated with shock wave effects (29), (30) and (31). The understanding of these effects is incomplete and some allowance must be made where they are considered likely to be relevant.

In considering these medium to large process volumes, the risk of cool flame autoignition requires to be considered. It is clear from the analysis of known ignition - volume effects that cool flame ignitions are only observable in volumes above a critical size and that they are more of a problem in large process vessels - see Coffee and D'Onofrio (18) and (19).

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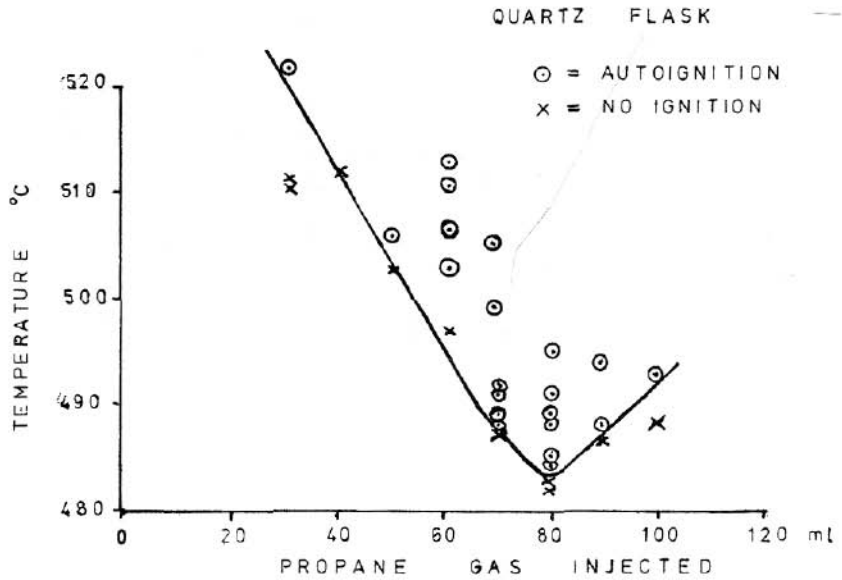


Figure 1 Typical standard autoignition results

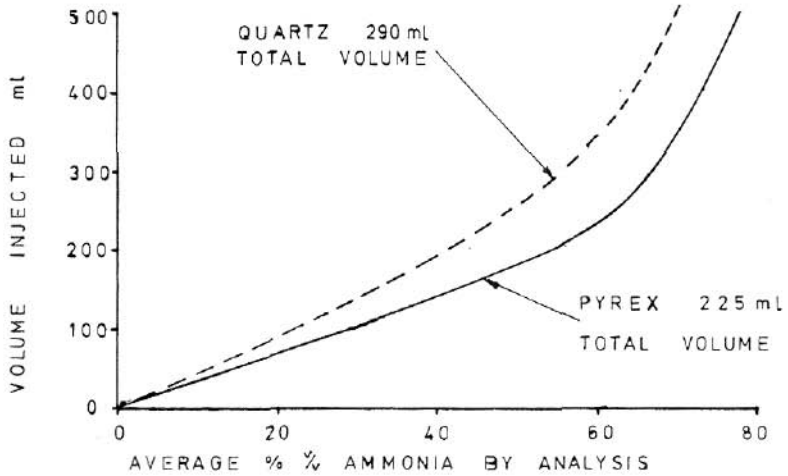


Figure 2 Room Temperature Ammonia Injection Average Compositions



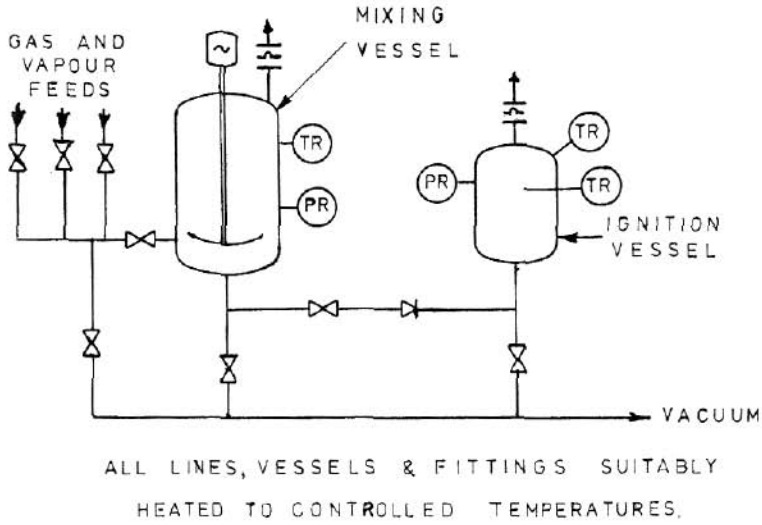


Figure 3 Autoignition Measurement for Specified Mixtures

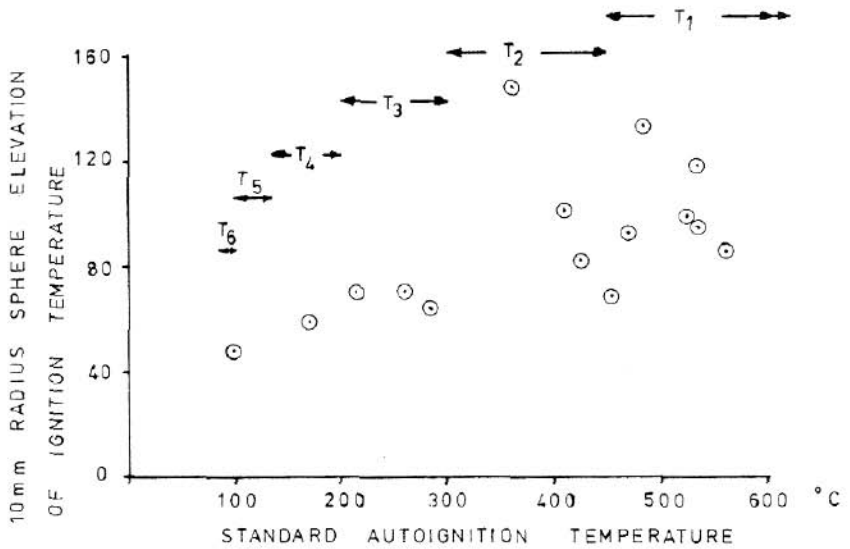


Figure 4 Small Volume Temperature Increase against Ignition Temperature