

COOL FLAMES – LABORATORY CURIOSITY OR INDUSTRIAL HAZARD?

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Cool flames have been known since the time of Sir Humphry Davy, and are often considered as a difficult to reproduce laboratory curiosity. However, a process re-assessed for fire and explosion hazards, prior to re-starting full-scale manufacture in a new reactor after a long break in manufacture, indicated that cool flames could not be precluded from being formed during the process as it was proposed. A study of the process conditions and reactor size concluded that air in-leakage under vacuum could promote the transition from a cool flame to a full explosion. Discussions with the manufacturing site about the potential to form a cool flame and the possibility of an explosion occurring if air were to ingress, produced a response that there had been an inexplicable rupture of a bursting disc on the reactor previously used for manufacture. The investigation at the time had not considered cool flames and had been unable to postulate a mechanism for failure of the disc. Reviewing the original investigation with the additional information on cool flames strongly suggested that a cool flame had been the ignition source responsible for the incident. Suitable precautions and modifications to the plant prior to manufacture are described.

INTRODUCTION

Certain compounds are capable of slow partial oxidation at mixture concentrations outside the normal flammability limits and at temperatures lower than those pertaining in normal combustion. This phenomenon is known as a cool flame and has been reported in the literature, particularly early on by Davy (1812) and Perkin (1882), who found that cool flames could be formed with a wide variety of hydrocarbons, alcohols and aldehydes. The cool flame has often been regarded as an unusual and esoteric laboratory curiosity, rather than a potential ignition source in industrial operations. An example of the higher concentrations and low temperatures for cool flames is shown in Figure 1.

Further work by Townend and Mandlekar (1933) re-discovered the phenomenon, and Hsieh and Townend (1939a, 1939b, 1939c) continued their work. Most other work on cool flames was driven by combustion theory rather than the hazard it posed for industrial-scale operations. It was work by D'Onofrio (1979), Coffee (1979), and Snee and Griffiths (1989) which indicated that industrial processes could be prone to autoignition by cool flames. There was much data on autoignition temperatures presented by Hilado and Clark (1972) and a discussion by Ashmore and Blumsom (1987) provided a background to the difficulties of the safe application of published autoignition temperatures in the open literature. However, there is a dearth on the propensity of individual

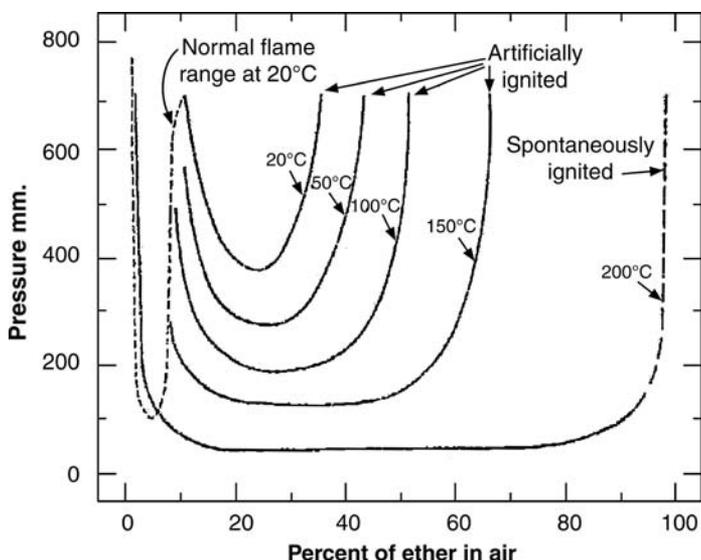


Figure 1. Cool-flame ranges of ether-air mixtures (from Hsieh and Townend 1939b – Reproduced by permission of The Royal Society of Chemistry)

substances to form cool flames. Thus the potential for cool flames to form in industrial-scale processes was already known, but like much obscure information, there has been a tendency to focus on the science rather than the practical application. This paper addresses a practical approach to dealing with the potential for cool flames to develop in an industrial process.

THE PROCESS

The process to manufacture a water-soluble polymer was submitted for an assessment of fire and explosion hazards. The original manufacture had been suspended some years before due to lack of demand, so it was thought prudent to re-visit the process prior to re-starting manufacture.

The process involved the use of a semi-solid polyester pre-polymer which is warmed to about 100°C to make it mobile enough to be pumped into the reactor. Once in the reactor, the reactor was inerted with nitrogen and heated up. At about 135°C, vacuum is applied to the reactor, and nitrogen is bled in to adjust the vacuum to control foaming. Starting at about 170°C, ethylene glycol is produced by the polymerisation, and starts to distil off. The pressure is maintained at about 100 mm Hg absolute using the nitrogen bleed. The temperature is allowed to rise to 270°C, and the pressure is

ultimately reduced to 20 mm Hg, signifying the end of reaction as no more ethylene glycol distills off. At the end of the reaction, the pressure is returned to atmospheric with nitrogen and the batch is cooled to 150°C, prior to being drowned out into hot water at 90°C to produce the final polymer solution.

FLAMMABILITY DATA

The pre-polymer had a flash point of $136 \pm 5^\circ\text{C}$, measured using the ASTM D3278-89 method. It had an upper flash point of $154 \pm 5^\circ\text{C}$, as measured according to the method of Hazegawa and Kashiki (1991). It was also tested for autoignition temperature using the IEC60079-4 test method (IEC, 1975), which uses a smaller flask than the ASTM E659-78 test (ASTM, 2000) so the results are not directly comparable, but the autoignition temperature was found to be 415–420°C.

The flammability data for the ethylene glycol by-product was taken from the NFPA (1986), with a flash point of 111°C, lower flammable limit of 3.2%v/v and an autoignition temperature of 398°C, but with no test method specified. Its electrical resistivity was determined by laboratory measurement at $3 \times 10^6 \Omega\text{m}$.

Finally, as the potential to form cool flames was possible with the ethylene glycol by-product, a test was undertaken using the IEC79-4 test, but with the flask maintained at 300°C. A cool flame was not noted at temperatures below 300°C in this test.

FLAMMABILITY ENVELOPE

During the process, it was identified that there would be a short period whilst heating the polymer where the temperature would be between the lower and upper flash point. As the reactor had been inerted with nitrogen, no flammable atmosphere would exist as there would be insufficient oxygen present to allow combustion to take place. However, once the vacuum was applied, it would be possible for air to leak in, and a flammable atmosphere could exist. In the early part of the process, there is a large amount of the ethylene glycol being vaporised, so the concentration would be likely to be over-rich, and there was a need to control the vacuum to prevent excessive foaming. To avoid air ingress, a nitrogen bleed was used rather than air.

However, once the majority of the ethylene glycol had been distilled off, the temperature would rise, typically to about 270°C, at an absolute pressure of between 100 and 20 mm Hg. This temperature is well above the flash point of the ethylene glycol, so the atmosphere could be flammable if air were allowed to enter, but if air were excluded then no explosion could occur. However, the reactor is under vacuum so there is the potential for air to leak in.

In examining the drawings for the U.S. made reactor, it was found that it had a maximum working pressure of 65 psig (4.5 bar gauge) at a temperature of 650°F (343°C), and had a gland fitted with PTFE vee rings. These are designed to seal against internal pressure, with the pressure spreading the vee so that the higher the pressure, the tighter the seal presses against the shaft. However, under vacuum, the vee tends to

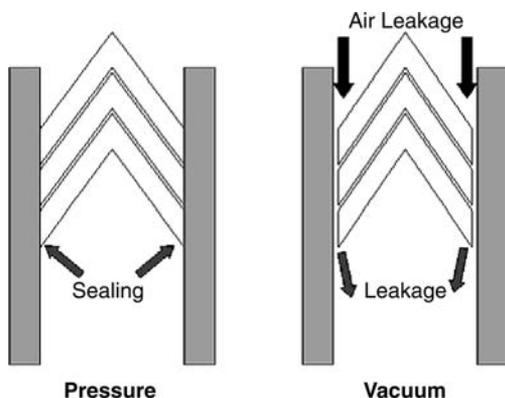


Figure 2. Loss of sealing of vee-rings under vacuum

close up, and the seal can leak inwards. This is illustrated in Figure 2. Note that in Figure 2 the gland base, lantern ring and gland follower are not shown to simplify the drawing. As the reactor was originally intended for use under pressure, this type of seal was perfectly satisfactory for a pressure vessel.

However, there was a strong possibility that air ingress would occur whilst under vacuum. It is unlikely that the air ingress would reduce the vapour concentration to below the upper flammable limit during the distillation, so long as there is sufficient ethylene glycol left to continue the distillation at the prevailing temperature. Whilst the atmosphere is above the upper limit, no explosion could take place, but it would be possible for a cool flame to form.

As the distillation approaches the end, the ethylene glycol concentration will gradually reduce, with the vapour concentration eventually coming into the flammable range. Under normal circumstances with a vapour which is not amenable to the formation of cool flames, such a process could be operated perfectly safely, by basing safety on the elimination of potential sources of ignition within the reactor. However, where there is the potential for a cool flame to form, such a basis of safety can no longer be used, as a potential ignition source cannot be eliminated.

COOL FLAME CONDITIONS

The potential to form a cool flame in a heated environment for ethylene glycol is discussed by D'Onofrio (1979). His work involved using several large flasks of differing volumes, enclosed in a heated chamber. The entire apparatus is used in a darkened room, so that the pale-blue luminescence of a cool flame can be observed. Using ethylene glycol, he determined the apparent activation energies from the time delay and temperature for both cool flames and autoignition, using flasks from 218 ml to 5.4 l. From the data for

four glycols (ethylene glycol, propylene glycol, neopentyl glycol and diethylene glycol), he determined an empirical equation of the form:

$$C_{FT} = m' \log V + C' \quad (1)$$

where

C_{FT}	= temperature at which cool flames occur, °C
m'	= constant
V	= vessel ullage, litres
C'	= constant

The coefficient of fit (r^2) for 38 data points for ethylene glycol was 0.92 giving values of -46.1 for m' , and 374 for C' . On the batch size and reactor size involved, this equated to a temperature at which cool flames can form of 251°C , which is well below the maximum processing temperature. Hence there is a distinct possibility that any in-leakage of air during the distillation would result in an atmosphere which, although over-rich, would produce conditions which would be conducive to the formation of cool flames. The plot of minimum cool flame temperature versus vessel size for ethylene glycol is unexpectedly steeper than those for the other three glycols, showing that cool-flame formation in ethylene glycol in larger vessels occurs at much lower temperatures. Consequently, it could be expected that cool flames could form within the reactor if air were to leak in, as the ullage space after the distillation was large, and the final temperature was high.

There were circumstances where in-leakage of air could reasonably be expected to occur, particularly under the circumstances of loss of vacuum. D'Onofrio (1979) cites examples of where ignitions have occurred in both laboratory and industrial situations, and no satisfactory explanation had been found. In view of this, he simulated the transition from cool flame to normal flame, by admitting air very slowly into a heated vessel containing a vapour under vacuum. A cool flame occurred, and once detected by a rise in temperature, air was admitted rapidly to bring the vessel up to atmospheric pressure. Almost immediately, the pressure and temperature both rose rapidly and an explosion occurred which was vented through the vessel top. Hence in the case of the reactor in this process, the same circumstances could occur if the vacuum pump were to fail and air ingress occurred.

SAFE OPERATION

Since the original gland packing was liable to leak air under vacuum, despite being leak-tight under pressure, it was necessary to change the seal to one which would not leak under vacuum. A mechanical seal suitable for an agitator shaft was specified. This type has two mechanical seals placed back-to-back, with the inter-seal space filled with a buffer fluid. A typical seal of a similar type is shown in Figure 3. The buffer fluid is pressurised to a greater pressure than that which would be expected within the reactor, so that loss of seal fluid pressure or level would indicate a leaking seal.

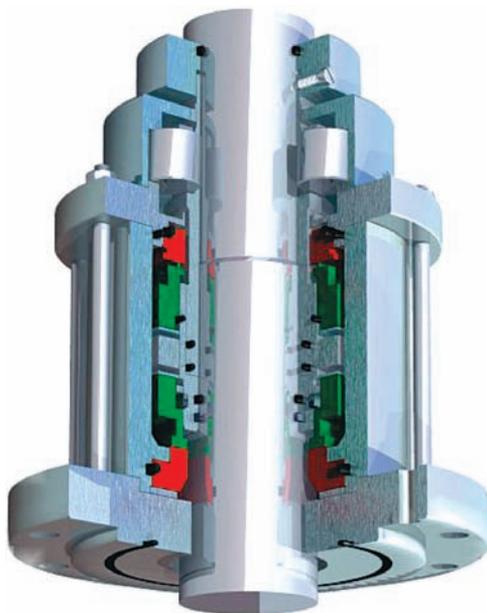


Figure 3. Typical double mechanical seal (Courtesy of John Crane UK Ltd)

On start-up, the reactor was pre-purged with nitrogen to remove oxygen, and the vacuum control was by nitrogen bleed rather than air. In order to reduce the consumption of nitrogen, the vacuum control valve was arranged to bleed gas from the vacuum pump exhaust back to the process, thus recycling the nitrogen, rather than bleeding fresh nitrogen in all the time. A small constant bleed was provided to the reactor to ensure that any air leaking in was suitably purged out of the reactor. Also, prior to starting the heating cycle, sufficient nitrogen was provided as a back-up to ensure that even if the supply of inert gas failed, there was sufficient nitrogen available to return the reactor to atmospheric pressure and cool it down safely.

At the end of the process, the vacuum was broken using nitrogen, and reactor was cooled to less than 150°C before drowning out into the water in the dilution vessel. As the ethylene glycol had been distilled off, the condensed glycol was cool enough to ensure that no cool flame would occur.

PREVIOUS INCIDENT

The potential for a cool flame to occur during this process was reported to the manufacturing unit who were preparing to operate the plant to make a batch of the polymer.

This was an unexpected and unknown hazard to them. However, after modifying the seal and vacuum system to make the operation safe, the manufacture was re-started. The works' personnel then realised that this mechanism could have been the cause of a rupture of a bursting disc which had hitherto not been explained to a satisfactory conclusion.

The original process had been operated in a vessel fitted with a 25 mm bursting disc set to operate at 2 bar, in a vessel with a working pressure of 4.5 bar, and a hydraulic test pressure of 9 bar. During the process, there had been a slow loss of vacuum whilst at high temperature, and after a period when the vacuum had risen to almost atmospheric pressure, the bursting disc ruptured. The original investigation team were unable to conclude why the disc had burst, and were not sure whether there had been an explosion or not within the vessel.

Having realised the possibility that a cool flame had occurred within the vessel, it became apparent that this was the most likely mechanism for an explosion since the vessel had been hot and under vacuum, and a slow leak had developed, admitting air. If a cool flame had been present, the slow increase in pressure would alter the partial pressure of oxygen, whilst the partial pressure of the ethylene glycol vapour would remain the same. Hence the originally over-rich vapour would slowly move into the flammable range. Once the mixture came below the upper flammable limit, a normal "hot" flame would then be able to propagate through the vapour space, resulting in an over-pressure. Assuming that the pressure was at about 0.6 bar absolute at the start of the explosion, a peak explosion pressure of about 7 times this would be expected, which would generate a pressure of 4.2 bar absolute, or 3.2 bar gauge. This is sufficient to rupture the bursting disc, but not to over-pressurise the vessel. Based on this hypothesis, it seems likely that a cool flame was the source of over-pressure which ruptured the bursting disc.

AUTOIGNITION VERSUS COOL FLAMES

It would appear that autoignition and cool flames are interrelated – except that cool flames are predominantly formed in over-rich or oxygen-lean systems and autoignition occurs where the flammable component is within its flammable range and there is sufficient oxygen for combustion. Snee and Griffiths (1989) demonstrate that the autoignition temperatures in vessels of different size are found to match a linear scaling relationship. The balance between heat generation by oxidation and heat loss from the vessel defines a critical temperature, above which autoignition occurs. However, as Snee and Griffiths (1989) state “...*the possibility that criticality leads to a cool flame rather than fully fledged ignition cannot be discounted...*” would reinforce the difficulty in determining whether a cool flame forms under all, some or few circumstances in hot, closed environments where fuel-air mixtures are present. Autoignition temperatures are relatively straightforward but tedious to determine. The propensity to form cool flames is not easy to determine, nor is the minimum cool flame temperature (C_{FT}).

APPLICATION TO OTHER PROCESSES

In this incident, the constants for use in D’Onofrio’s formula given in Equation (1) above were available from his paper. In many processes these constants may be unavailable. It is known that a cool flame is difficult to see, but thermal imaging cameras can be used to view the equipment under normal ambient lighting conditions. The development of a cool flame viewed by a thermal imaging camera at the Health and Safety Laboratory at Buxton is shown in Figure 4. This shows the formation of a hot kernel developing into a cool flame passing upwards into the mixture, without propagating throughout the entire vessel.

The greatest problem in identifying the potential for cool flames is determining whether or not the material is susceptible to their formation. There appears to be no easy way of determining whether a material can form cool flames or not, although there are some chemical species and groups which are more prone than others.

Those materials reported as forming cool flames are glycols by D’Onofrio (1979); and hydrocarbons, alcohols, aldehydes, oils, acids, and waxes by Perkin (1882). However, according to Coffee (1979), the fundamental differences between autoignition and cool flames are as follows:

Parameter	Cool Flame	Autoignition
Temperature rise ΔT	10–150 K	800–1200 K
Confined volume pressure rise ratio	<2	6–8
Combustion products	CH ₂ O, CO	H ₂ O, CO ₂

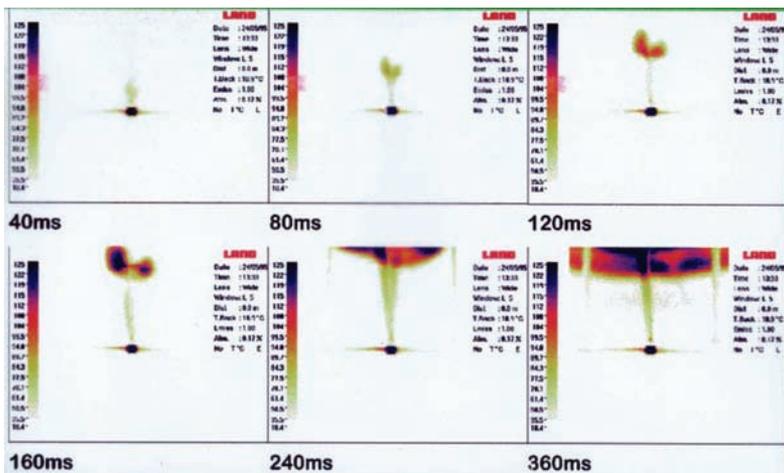


Figure 4. Development of a cool flame in diethyl ether vapour

Whilst the autoignition temperature of a combustible material is measurable, and there is plenty of data in the open literature, the equivalent data on cool flames is not readily available. If a material is prone to oxidation, then it is self evident that cool flames are more likely to occur, but the prediction of the temperature at which a cool flame may occur cannot be predicted without some experimental data.

Further work, which appears not to have been reported directly (Coffee, 1979) shows that autoignition temperatures for many materials form a straight line on logarithmic co-ordinates with volume, all converging at a volume of 10^{15} m^3 and a temperature of about 348 K. Whilst this refers specifically to autoignition, the phenomenon of cool flames is closely related, and the equation due to D'Onofrio also exhibits a similar logarithmic dependency on volume. However, there appears to be no converging temperature, thus leaving it difficult to estimate a suitable minimum temperature at which a cool flame may occur.

CONCLUSIONS

- Cool flames are not simply a laboratory curiosity, but a real hazard in high temperature processes in industry.
- The potential to form cool flames is difficult to predict, but guidance is available on the types of materials which may result in cool flames.
- Where cool flames may occur under vacuum, ingress of air can lead to a normal flame and hence an explosion occurring.
- An assessment of fire and explosion hazards should include the potential for the formation of cool flames.
- Where there is a potential to form cool flames, a suitable means of preventing oxygen ingress should be incorporated into the process to ensure that transition cannot occur from cool flame to normal hot flame, with the resulting potential to create an explosion.

NOMENCLATURE

C_{FT}	= temperature at which cool flames occur, °C
m'	= constant
V	= vessel ullage, litres
$C \pm$	= constant

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