



The relation of cool flames and auto-ignition phenomena to process safety at elevated pressure and temperature

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Abstract

The cool-flame phenomenon can occur in fuel–oxygen (air) mixtures within the flammable range and outside the flammable range, at fuel-rich compositions, at temperatures below the auto-ignition temperature (AIT). It is caused by chemical reactions occurring spontaneously at relatively low temperatures and is favoured by elevated pressure. The hazards that cool flames generate are described. These vary from spoiling a product specification through contamination and explosive decomposition of condensed peroxides to the appearance of unexpected normal (hot) flame (two-stage ignition). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Auto-ignition; Slow oxidation; Cool flames; Explosion; Two-stage ignition

1. Introduction

Partial oxidation processes, carried out at elevated conditions, are widely used in the chemical industry. Propylene oxide, ethylene oxide, methanol, and phthalic anhydride are examples of versatile, widely applied petrochemicals that are produced by partial oxidation at elevated temperature and pressure. Table 1 lists some process conditions; the highest values are marked by bold characters. Such extreme conditions demand rigorous safety considerations. Due to these conditions, explosiveness increases as flammability limits become wider, while minimum ignition energy and auto-ignition temperature (AIT) decrease. Detailed knowledge about relevant explosion indices is essential for operating not only safely, but also in the *economically* most efficient way. Such explosion indices must be

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Table 1
Process conditions for several processes in the chemical industry

Process unit/vessel	Temperature range (°C)	Pressure range (bar)
<i>Chemical processes</i>		
Partial oxidation	150–400	1.5–120
Catalytic partial oxidation	750–900	50
Catalytic reformers	425–540	69
Hydrocrackers	425–480	69–276
Hydrodealkylation	595–760	55–83
Hydrodesulfurizers	425	1.0–103.5
<i>Coal conversion processes</i>		
Solvent refined coal	370–540	0.7–689.5
Pyrolysis	230–875	1–379
Gasification	260–1815	1–310

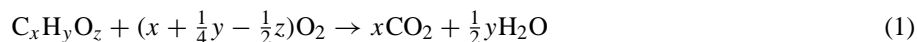
known under realistic process conditions, thus at (high) temperature, (high) pressure (and high turbulence) conditions, as are encountered in practice.

However, the explosion indices mentioned above, which are essential for design and safety assessment, are not complete. It is, for example, widely believed that a fuel-rich, flammable mixture kept below its AIT in process apparatus cannot ignite and therefore cannot explode. Unfortunately this is not always true, since phenomena like cool flames may lead to unwanted side-reactions and, in the worst case, to explosion. The resulting by-products may spoil the quality of the main product through contamination. The process in which a cool flame is followed by ignition so that explosion occurs is called ‘two-stage ignition’.

Indeed, any review of so-called “unexplained” industrial losses will quickly uncover numerous incidents, which can be explained as possibly being due to the initiation of cool flames with subsequent transition to a hot ignition.

2. General combustion kinetics

Any combustion reaction of hydrocarbons in air or oxygen is not a one step oxidation process leading to the final products (typically carbon dioxide and water). In reality the mechanism of the process involves many intermediate compounds, like carbon monoxide, aldehydes, ketones, alkenes and oxygenated species. The general oxidation, scheme (1), shows the overall reaction but contains absolutely no information about the intermediate steps the oxidation mechanism goes through as the fuel is converted to the final products.



The general oxidation reactions can be divided into three mechanisms, namely: *initiation*, *propagation* and *termination*.

In the initiation stage, fuel is converted into radicals:



or



where RH denotes any hydrocarbon and R^\bullet is its radical. At low temperatures, formation of the HO_2^\bullet radical is favoured. However, at low temperature the reaction rate of reaction (3) is much lower than for reaction (2), so the initiating oxidation reactions occur mainly through reaction (2). The lowest temperature at which the H-abstraction reaction may occur is about 140 °C, in case of aldehydes, since the bond strength between the carbon and hydrogen atom is the weakest. In case of alkanes, the rank of bond strength is as follows: weakest is a tertiary carbon atom, then a secondary carbon; strongest is a primary carbon atom. Additionally to reactions (2) and (3), especially higher alkanes (C4 or higher) may also decompose thermally forming two alkyl radicals.

After undergoing the primary oxidation reaction, in which only compounds initially present in the mixture participate in reactions, there is a secondary oxidation reactions in which already formed compounds react together and with unconverted fuel:



where X represents, depending on conditions, H^\bullet , $\bullet\text{OH}$, O^\bullet and HO_2^\bullet radicals forming H_2 , H_2O , $\bullet\text{OH}$ and H_2O_2 , respectively.

When initially radicals are formed, they react with other compounds present in the mixture (*propagation*) by a *straight chain* or a *chain branching* mechanism. In a straight chain reaction, one radical reacts with a stable molecule creating another stable molecule and one (other) radical. In a chain branching reaction, two radicals are formed for each radical consumed. Since both mechanisms are present during oxidation, the multiplication factor, mostly denoted as α , has a value in the range between 1 and 2. It is very important to emphasise the difference between the effects of the mechanisms mentioned. We can express the time needed for full conversion by dividing the number of needed collisions by the frequency of the collisions. Let us consider a 1 m³ vessel kept at 300 °C and 1 bar. Assuming in the vessel only one active molecule initially, one can calculate the reaction time for straight chain propagation mechanism as 6.02E + 15 s, this is 190E + 6 years. If, by contrast, a pure chain branching reaction mechanism is assumed, the multiplication factor α equals 2. For full consumption of the reactants, we need 83 number of steps and the conversion time is 3.97E – 8; this is about 40 ns [1,27].

In reality these two reaction mechanisms occur simultaneously, and some radicals are *terminated*. Assuming α equal to 1.001, one can calculate, the number of steps is 57 827 and the time for consumption is 27.5 ms.

From this comparison one concludes that the occurrence of chain branching reactions greatly shortens the oxidation time relative to that occurring via straight branching reactions. Moreover, if only one radical is formed in the system capable of undergoing branching reactions and if within the branching reactions there is at least one chain branching step and if no termination reactions occur, then the system is likely to convert all fuel and to be explosive.

When the rate of radical formation is lower than the rate of radical termination of newly formed radical, the *termination* stages begins, and the oxidation reaction ceases.

It should be stressed that, although the general *oxidation chemistry* of alkanes is reasonably well understood, many detailed aspects are still under speculation. The oxidation

proceeds through many intermediate compounds prior to the formation of the final products. These intermediates, whose formation is more pronounced at low oxygen concentrations and low temperatures, include aldehydes, ketones, alcohols, O-heterocyclic compounds, alkenes, peroxides, and carbon monoxide. They play an important role in the peroxy oxidation chemistry regime.

One can generally state that the oxidation chemistry of hydrocarbons depends on temperature, pressure and oxygen contents of the system. The oxidation path with respect to temperature can be divided into:

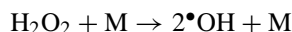
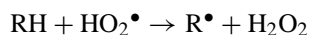
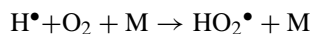
- A low temperature regime, where peroxy oxidation chemistry occurs;
- An intermediate temperature regime, where HO₂ and H₂O₂ chemistry dominates;
- A high temperature regime, where small size radical chemistry occurs.

Examples of dominating chain branching reactions in these regimes are [2]:

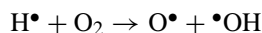
- *Low* temperature oxidation mechanism:



- *Intermediate* temperature oxidation mechanism:



- *High* temperature oxidation mechanism:



O[•] and [•]OH radicals are very reactive and, therefore, generally do not react selectively with other molecules. In contrast R[•] and HO₂[•] radicals are much less reactive, and one may consider them as termination radicals.

Let us look at the low temperature oxidation mechanism, which is commonly present in the chemical industry. At low temperature, the alkyl radical R[•] reacts with an oxygen molecule (5) forming a peroxy radical. At high temperatures, the equilibrium is shifted to the left, preventing the formation of peroxy radical.



Therefore, the low temperature oxidation path ceases at higher temperature. However, if the temperature remains below about 450 °C at 1 bar, the peroxy radical is formed, and the oxidation mechanism occurs as presented in Fig. 1 [3,4]. It should be emphasised that the temperature limits are dependent on fuel molecular structure and system pressure. Increasing pressure favours the low temperature oxidation mechanism, and so at higher pressure low temperature oxidation mechanism will dominate even at higher temperature.

The alkyl radical R[•] may thermally decompose giving a smaller alkyl radical and an alkene, or it may react with oxygen. Reaction with oxygen produces either the HO₂[•] radical and an alkene containing the same number of carbon atoms as the alkyl radical, or the

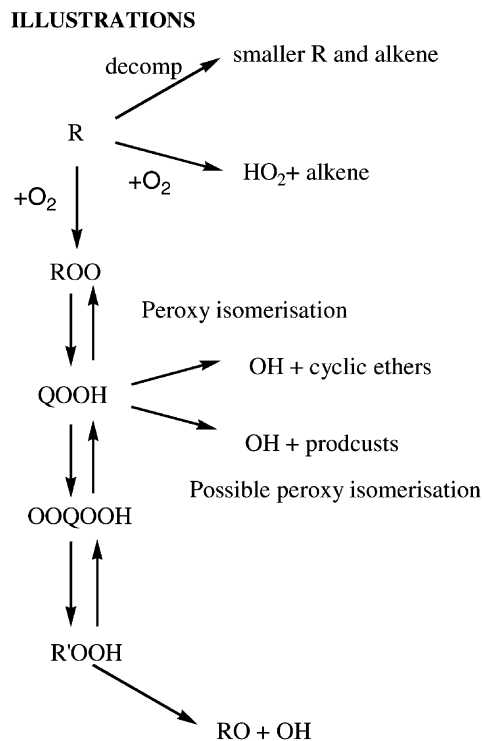


Fig. 1. Simplified alkane low temperature oxidation mechanism.

alkylperoxy radical ROO^\bullet . The alkylperoxy radical undergoes *peroxy isomerisation*. During this process, hydrogen is transferred internally to form the hydroperoxide group ($-\text{OOH}$) and a new alkyl radical centre.

After that, the molecule is denoted as QOOH. QOOH may contribute to the propagation stage by decomposition to an $\bullet\text{OH}$ radical and further products (e.g. aldehydes), or it may undergo a cyclisation process forming cyclic ethers.

At low temperature, QOOH may add molecular oxygen to form hydroperoxy-alkylperoxy radicals, $\bullet\text{OOQOOH}$ [5,6]. Finally, this radical may abstract HO_2 , forming $\text{R}'\text{OOH}$, which is a degenerate branching agent. It decomposes into two radicals resulting in rapid multiplication in the number of radicals [7].

3. The cool-flame phenomenon

3.1. Introduction

The reactions of hydrocarbons and air at low temperature, which occur after an induction period, accompanied by a pale blue chemiluminescence was first reported by Humphry in 1812 [8]. In 1929, Emeleus [9] used the name 'cool flames' to describe the weakly

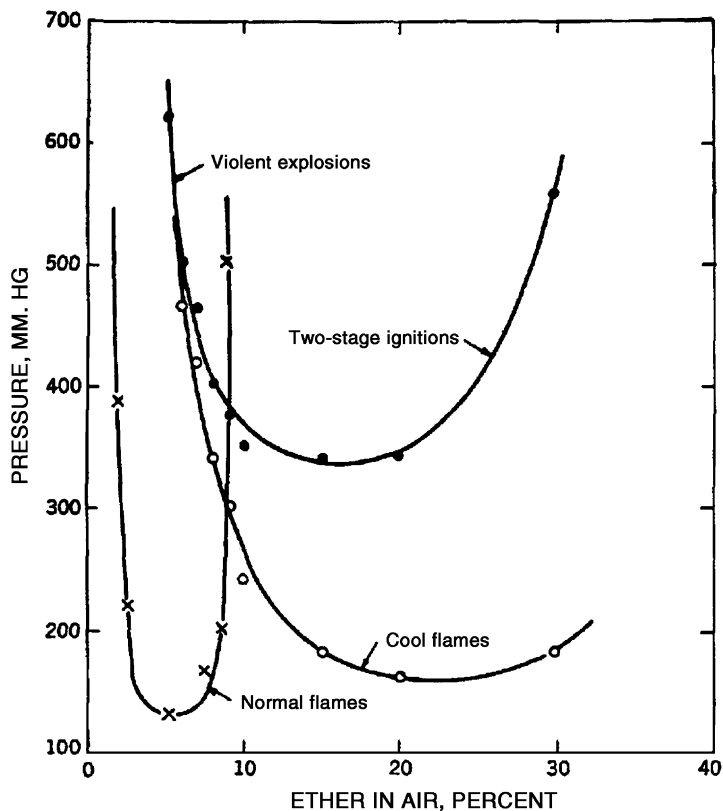


Fig. 2. Flammability diagram for diethyl ether/air mixtures as a function of pressure.

luminous flame that gave the same emission spectrum, regardless of fuel. The same spectrum was observed for different hydrocarbons (saturated and unsaturated), alcohols, aldehydes, ketones, acids, oils, ethers and waxes. In the past, a fuel whose capability to exhibit cool flame was questionable was methane. However, recent publications proved the existence of cool flames even for methane [10–12].

Cool flames are associated with the low temperature gas phase oxidation (gases and vapours) of an organic substance in air or oxygen in a fuel-rich region both within the flammable range and above the upper explosion limit (see Fig. 2).

Typical values of temperature increase are up to 200 °C; the highest value observed is 400 °C [13,14]. Similarly, the pressure pulses developed in confined spaces are small compared to those generated by normal flames and typically do not exceed twice the initial pressure. At certain conditions, several consecutive cool flames are observed in the system. For a given fuel concentration, an example of envelopes of multiple cool flame is given in Fig. 3. Shape and borders of the envelopes depend on fuel concentration, molecular structure, vessel shape and size (surface to volume ratio), wall conditions, and heat transfer.

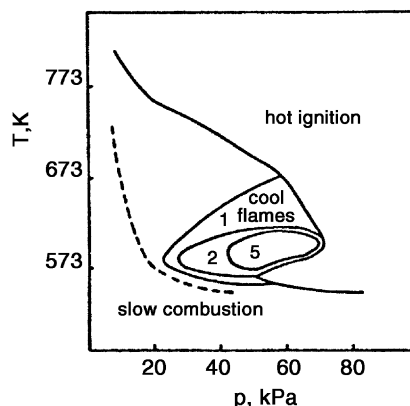


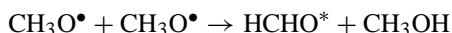
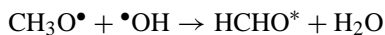
Fig. 3. The ignition diagram of a propane/oxygen (1:1) mixture [15]. The numbers 1, 2, and 5 refer to the number of cool flames occurring in the respective region.

The cool-flame temperature (CFT) is reported as the lowest temperature at which the pale blue luminescence can be visually observed. The CFT is significantly lower than the AIT (see Table 2).

Cool flames have been reported in dynamic systems such as combustion engines [2,16–18] and, flow tubes, as well as and static systems [10,13,19].

3.2. Visual appearance and products formed

In 1926 Emeleus [20] first recorded the emission spectrum of the cool-flame phenomenon. The emission spectrum appeared to be the same for several different fuels. The spectra of cool flames consist of a series of bands, shaded toward the red, the intensity of which is greatest in the blue and near-ultraviolet regions. The blue luminescence originates from an electronically excited state of formaldehyde, which is formed in a chemiluminescent reaction mainly by the radical + radical reactions:



Additional emission sources might be present, but their contribution to emission is very minor compared to formaldehyde chemiluminescence [14,21,22].

Table 2
Comparison between CFT and AIT (NFPA 325 M [13])

Compound	CFT (°C)	AIT (°C)
Methyl ethyl ketone	265	515
Methyl iso butyl ketone	245	460
iso-Propyl alcohol	360	400
n-Butylacetate	225	420

The sequence of temperature increases before the appearance of a feeble pale blue glow, the increase in its intensity, the appearance of a cool flame, its disappearance, and finally the onset of ignition of a normal flame is the same for all hydrocarbon fuels investigated. The absolute value of these temperatures in the case of fuel-rich mixtures varies slightly with the ratio of fuel to air. For the series of paraffin hydrocarbons, these temperatures decrease with increase in the molecular weight of the hydrocarbon.

A wide variety of stable and moderately stable products is created after the cool-flame phenomena occur. In case of alkanes, these are alkenes, alcohols, saturated and unsaturated aldehydes and ketones, and O-heterocyclic compounds. In addition, water and oxides of carbon are formed, the concentrations increasing with the availability of oxygen. With increase of temperature, the yields of oxygenated organic products gradually decrease, while those of alkenes and of hydrogen peroxide increase.

Because aldehydes and carbon monoxide are formed (among many other products), rather than the water and carbon dioxide produced by normal combustion flames, cool flames are often referred to as the phenomena associated with partial or intermediate oxidation reactions.

3.3. *Effect of pressure and temperature*

In hydrocarbon–fuel mixtures, for each temperature in the cool-flame zone, there is a certain critical initial pressure above which cool flames arise following an induction period. Below the critical pressure, cool flames are not formed (see Figs. 2 and 3). The induction period of a cool flame is defined as the time from the introduction of the mixture into the reaction vessel until the cool-flame luminescence starts. Inside the cool-flame zone, an increase in temperature for a certain constant initial pressure is accompanied by a decrease in the induction period and increase in intensity (brightness of luminescence, magnitude of pressure increase) of the cool flame. Further increase in temperature results in an even greater decrease in the induction period, but with a decrease, instead of an increase, in intensity of the cool flame. This effect is due to the disappearance of the peroxy radical (reaction (5)), whose presence is necessary for the further low temperature oxidation path. If, on the other hand, the temperature is kept constant and the pressure is increased progressively, then the duration of the induction period falls continuously and the intensity of the cool flame increases (Fig. 4). This effect is due to the fact that the low temperature oxidation path thus cool flames are favoured by increasing pressure [16–18].

Since reactions leading to the cool flame are not isothermal, obviously the greater the volume, the shorter the induction period, since relative heat loss decreases as vessel size increases.

3.4. *Two-stage ignition phenomenon*

During the cool-flame induction period, a slow oxidation process occurs leading to the consumption of only insignificant quantities of the initial reactants. In a cool flame the extent of oxidation usually reaches 50%, so that the products contain about 50% non-oxidised hydrocarbon, 30% aldehydes, 10% peroxides and a more or less significant remaining concentration of the initial oxygen. In this mixture, reactions can occur involving both

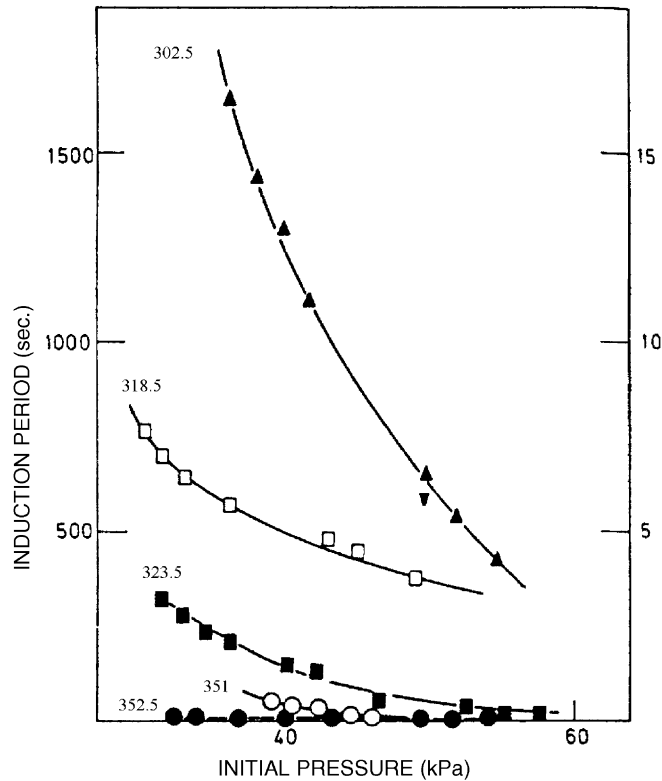


Fig. 4. The dependence of the induction period for a cool-flame phenomena on initial pressure and temperature of an *iso*-butane/oxygen (1:2) mixture. The system temperature is shown close to the relevant curves (modified after [19]).

further oxidation of oxygen-containing compounds and oxidation of the hydrocarbon. With increase in the initial pressure, both the rate of these reactions, the quantity and rate of heat evolved increase. If the pressure exceeds a certain critical pressure, the rate of heat production exceeds the rate of heat loss; thus, a breakdown occurs in the heat balance, and hot ignition takes place. Since the cool flame preceded this ignition, the whole process has a two-stage character and is called *two-stage ignition* (Figs. 2 and 6d–f).

Important to note is that the products of the second stage (hot flame) are very different from those of cool flames. During the highly exothermic second stage of ignition, the wide variety of oxygenated products produced in the cool-flame stage are largely destroyed. The concentrations of water, oxides of carbon, and of low molecular weight hydrocarbons increase. In fuel-rich mixtures, extensive cracking of the excess fuel occurs, giving high yields of simple aliphatic and of aromatic hydrocarbons and, in very rich mixtures, depositing soot.

Concerning fuel concentration in the mixture, there are two possibilities of transition from cool flame to hot ignition (see Fig. 2). In the first, the fuel concentration is within the flammable range, close to the upper explosion limit. In the second case, the mixture is kept above, but still near to, the upper explosion limit. The temperature and pressure of the

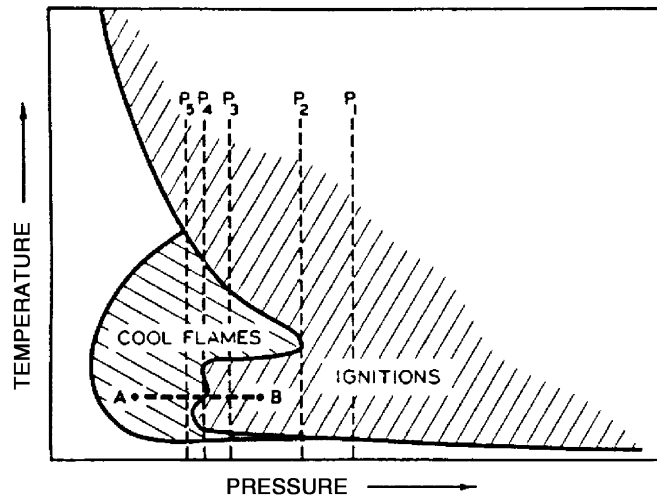


Fig. 5. Typical ignition diagram for fuel concentration within the flammable range.

mixture increase due to cool-flame phenomena, widening the flammability range. When the flammability region is thus entered, an explosion may take place. This is illustrated in Fig. 5 on a typical ignition diagram. At some pressure, P_5 , the heat generated by cool flames is sufficient to rise the temperature to the ignition point. Increase in pressure causes the same effect: shift from point A to B in Fig. 5. Since in closed systems the cool flame increases both temperature and pressure, the resulting direction of change will be upwards, not parallel to either the temperature or pressure axis [13,19,23].

Moreover, intermediate compounds created during the induction time and products of cool flames have higher upper explosion limits than the fuel. Such a situation is likely to happen in continuous processes, where the oxygen concentration is constant. Due to the contribution of these more flammable gases, the upper explosion limit of the mixture increases, and—very importantly—the flammability range becomes wider: the system has become more hazardous.

4. Possible phenomena at low temperature oxidation

At low temperatures, several oxidation phenomena have been observed, like a single cool flame, successive cool flames (up to seven [19]), two-stage ignition, and multiple-stage ignition [24]. These are presented in Fig. 6.

For experiments presented in Fig. 6, a spherical Pyrex glass vessel of volume 500 cm^3 was used with the mixture of *iso*-butane and oxygen at a ratio of 1:2. Below 340°C (line a), the pressure rise generated by these cool flames is transient, and the pressure falls almost to its initial value after passage of each successive cool flame. Between 340 and 350°C , the transient pressure pulses are smaller and are superimposed upon continuous pressure increase due to slow combustion (line b). Above 350°C , only one cool flame propagates, but its build-up is much faster (line c) than the previous cases. Two-stage ignition (lines d–f)

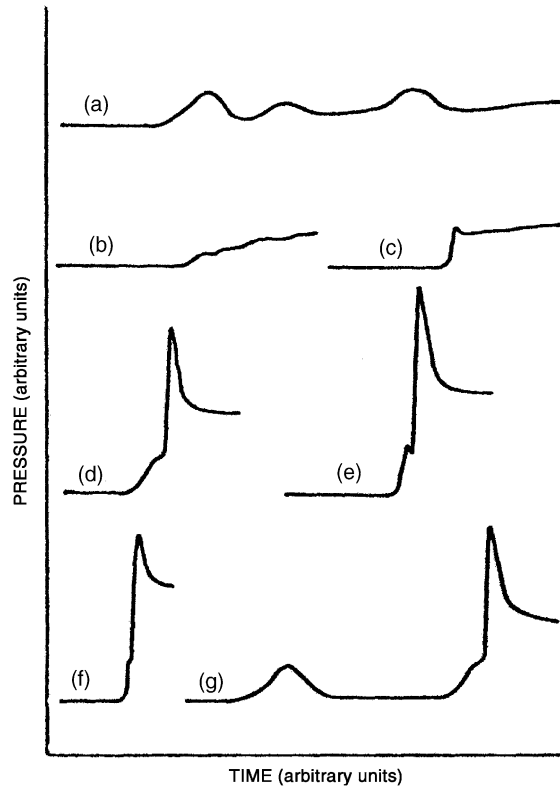


Fig. 6. Pressure versus time for an *iso*-butane/oxygen mixtures (1:2) [19].

with and without intermediate pressure decrease are observed above 350 °C and high initial pressure (>ca. 51 kPa). Additionally, a three-stage ignition is observed at high pressure and temperatures starting from 310 °C (line g). At temperature higher than 410 °C, auto-ignition always occurred.

5. Safety aspects—accidents

Since cool flames generate only minor temperature and pressure changes, in themselves they do not present a significant hazard. However, products formed and mixed with the chemicals in a given process may lower the final quality of the products through contamination. Build-up of peroxides during the induction period can create additional safety problems. Peroxides can decompose explosively, and if they manage to accumulate, they may lead to damage causing loss of containment and may even serve as an unexpected ignition source. Accumulation may occur either in ‘dead spaces’ or due to condensation in cold spots within the equipment, the latter since peroxides have much higher boiling points than their precursor hydrocarbons.

Table 3
Comparison between cool-flame phenomena and flames in normal combustion

Parameter	Cool flames	Normal flame
ΔT (°C) (in air)	10–200 (400)	1600–2700
P_e/P_0 (in confined spaces)	Below 2 (low)	6–11 (high)
Flame velocity (cm/s)	3–8	30–80
Flammability range	Wide	Narrow
Heat liberation	Low	High
Temperature coefficient	Negative	Positive
Typical products	CH ₂ O, CO	H ₂ O, CO ₂

Additionally, there is the danger of explosion induced by appearance of a cool flame (two-stage ignition), as shown in Figs. 5 and 6d–g. Temperature pulses associated with pressure changes may also promote transitions to ignition. A comparison between the effects of normal flames and cool flames is given in Table 3.

D'Onofrio [23] described several accidents in which cool-flame phenomena was the cause of explosion. One of them refers to a distillation process. Long-chain fatty acid was distilled in a distillation column operating under vacuum (50–100 mm Hg), at above 200 °C. The column was shut down and opened to air. As soon as pressure in the vessel reached atmospheric, or very shortly after, the manhole at the bottom of the column was opened. A huge flame jet erupted, and several workers were severely burned. The trays in the column were demolished. Apart from human injury and process damage, the accident also caused significant business interruption.

6. Conclusions

We have shown that the general practice of operating below the AIT does not always guarantee safe operation since cool flames can occur leading to hot ignition. On the basis of the information presented, the following general conclusions may be presented:

- For a given compound in air or oxygen, cool flames may occur at temperatures hundred of degrees lower than the AIT of that compound (see Table 2).
- Cool flames can be initiated by a process disturbance, e.g. hot spots.
- Cool flames may lead to explosion by so-called two-stage ignition.
- Pressure increase promotes the occurrence of low temperature oxidation chemistry, which can lead to cool flames and two-stage ignition.
- Temperature and/or pressure increase shortens the induction time for cool flames. However, above a certain temperature cool flames will not appear.
- Products of cool flames and of the low temperature oxidation mechanism increase the upper explosion limit, thus making the system more hazardous.
- Formed peroxides (induction period) may condense in the system and accumulate, leading to increased risk of ignition and/or even possible explosion.

Possible dangerous situations may occur if:

- Process conditions are within the cool-flame regime.

- Residence time in the process equipment, for example due to ‘dead spaces’, exceeds the induction time for cool flames. Such conditions may occur, for example, during shutdown of the process.
- Hot spots are present within process equipment. Such spots locally increase the rate of oxidation processes, thus increasing the concentration of active intermediate compounds. Cold spots also exist in process equipment, allowing condensation of peroxides. Their explosive decomposition may lead to damage causing loss of containment and may further serve as an ignition source.

In summary, CFT and limits should also be considered as a safety parameter for processes operating at elevated temperatures and pressures.

For further reading see [25,26,28].

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