Sensitization of Pentane-Oxygen Mixtures to DDT via Cool Flame Oxidation

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Introduction

The detonation wave in an explosive gaseous mixture in a vessel can be initiated by an accelerating flame ignited at one end of the tube and propagating towards the other end. The ability of the deflagration to accelerate and transit to a detonation (DDT for deflagration to detonation transition) depends on the parameters that determine sufficiently high burning rates. These are achieved by the rapid mixing between hot combustion products, active free radicals and unreacted mixture, through various mechanisms [Lee, 1985]. The pre-detonation distance, or "run-up-distance", travelled by the accelerating flame before transition, depends on the ability of the mixture of readily generating free radicals. For this reason, the run up distance represents an experimental measure of the sensitivity of a detonable mixture. The shorter is the run up distance, the more sensitive is the mixture with respect to detonation.

The present work investigates the sensitization of a pentane-oxygen mixture by addition of free radicals via "cool flame" oxidation process.

An important feature of hydrocarbons combustible mixtures is that they present a two-stages ignition mechanism at rather low temperatures. This mechanism involves the appearance of cool flames, or partial oxidation of the fuel, that generates peroxides radicals. When the concentration of these free radicals reaches a critical value, they decompose liberating a small amount of energy accompanied by light emission. This is the phenomenon of "cool flames".

Therefore, the cool flame process determines a profound change of the chemical characteristics of the mixtures with a large increase of the concentration of free radicals necessary to start the combustion reaction. In fact, Bonner and Tipper[2] in 1965 pointed out a maxima in the concentration of peroxides simultaneous with the appearance of cool flames. For this reason, it would be expected a maxima of the sensitivity of the combustible mixture at the instant of onset of cool flame or immediately before.

This possibility was investigated by Sokolik[3] that, in 1937, showed a significant reduction of run up distance to transition from deflagration to detonation when a pentane-oxygen mixture was undergoing cool flame oxidation prior to spark ignition. However, this experiment was never repeated and therefore the conditions for maximum sensitivity of the mixture were never established.

The objective of the present investigation is to reproduce Sokolik's experiments and confirm his finding that cool flame oxidation can lead to a significant reduction of the run up distance to transition from deflagration to detonation.

Experimental Details and Results

Figure 1 illustrates the apparatus used during the investigation. A glass detonation tube 120 cm long and 2.4 cm inner diameter was heated by heating tapes while the temperature was monitored by E-type thermocouples glued on the outer surface of the tube. The detonation tube was enclosed in a aluminum tube provided with a slit 2 cm wide to allow photographic (streak) recording of the flame propagation. A "Shchelkin spiral" was inserted in the tube to promote reproducible transition distance to DDT within the first half of the length of the tube. The spiral had a pitch of 1 tube diameter and determined a blockage ratio of 0.09. The n-pentane-oxygen mixture ($\phi = 1.1$) was prepared before each test by vaporizing the fuel in a previously evacuated stainless steel mixing chamber and then oxygen was added according to the method of partial pressures. The mixing chamber was provided with a heating element to keep the

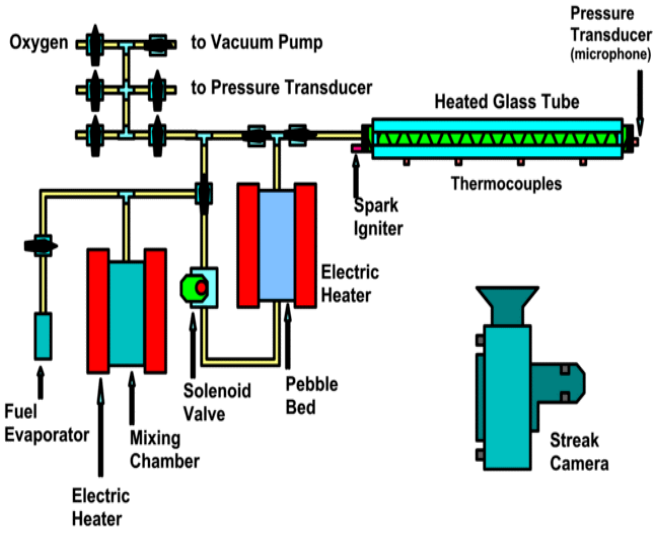

Fig. 2 Schematic of experimental apparatus.

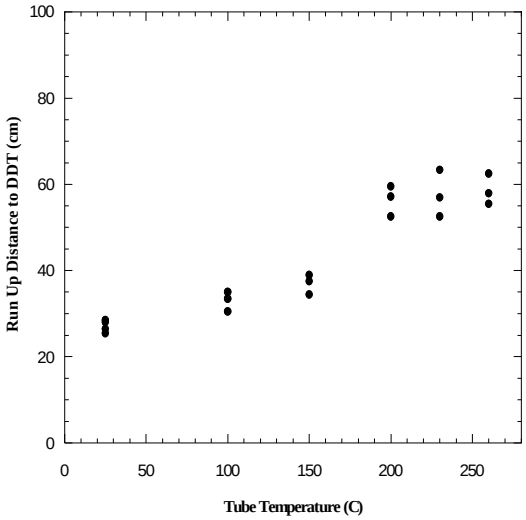

Fig. 2 Run up distance versus temperature of heated tube.

temperature at 50 °C creating convective mixing of the fuel and oxidizer. The mixture was injected in the evaquated detonation tube by opening a solenoid valve. Between the mixing chamber and the detonation tube, a heated pebble bed provided adequate mixing and pre-heating to the mixture. This pre-heater consisted of a packed bed of 1/4 inch stainless steel spheres in a 1 liter capacity stainless steel vessel. This configuration proved to be useful to obtain a more uniform temperature of the mixture and to reduce its residence time in the heated detonation tube before the appearance of a cool flame. The onset of cool flame could be monitored by a 50 μm thick K-type thermocouple located along the axis of the tube, 7 cm from the inlet. On the other end of the tube, a pressure transducer monitored the pressure of the mixture. The mixture was ignited by a weak spark on the side of the inlet

This apparatus was used to investigate the detonation inside a heated tube where temperatures in the "cool flame region" could be attained. Subsequent to the onset of cool flame, the mixture was spark ignited and run up distance was measured from the photographic recording (streak photography).

The investigation was divided into three main experiments: 1) Verification of the effect of temperature (without cool flame) on the transition distance to DDT. 2)Determination of the delay of onset of cool flame with respect to the temperature of the heated tube. 3) Verification of the effect of cool flame on transition distance to DDT when the mixture was spark ignited at different instants with respect to onset of cool flame.

1)Effect of temperature on run up distance to DDT.

A series of tests permitted to determine that the minimum tube temperature for onset of cool flame was just below 300 °C at the working pressure that was fixed at about 26 KPa. This pressure value was obtained by filling the mixing tank, at 50 °C, with 40 KPa of combustible mixture. This amount of mixture was used for each test throughout the whole investigation.

After waiting a few minutes to ensure mixing of the fuel and oxidizer, the solenoid valve was opened and the mixture was passing through the pre-heater and filled the tube. Subsequent to an initial transient, the gas reached the final temperature within 2 sec from the instant of opening of the solenoid valve (time of injection). The pressure transducer (response time 1ms.) showed that 99% of the final pressure was reached after about 0.5 sec from injection. The pressure transducer was not sufficiently sensitive to detect the faint pressure wave (reported by Sokolik) that accompanied the onset of cool flame. A series of shots were fired maintaining the temperature of the tube at temperatures below the temperature of onset of cool flame to determine the effect of temperature alone (without cool flame) on the run up distance to DDT. Figure 2 shows the dependence of the transition distance with respect to tube temperature up to

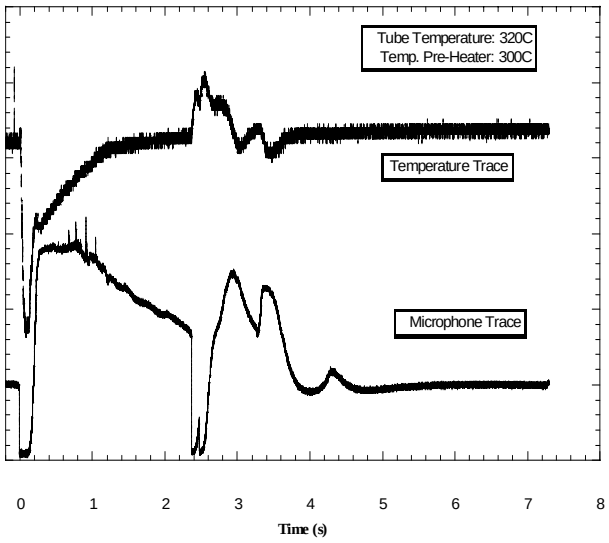

Fig.3 Thermocouple and microphone traces at onset of cool flame.

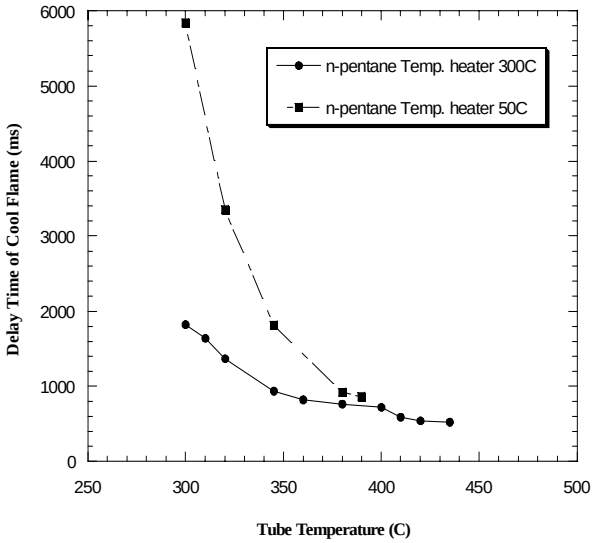

Fig.4 Delay time of onset of cool flame with respect to tube temperature.

280 °C. All the shots were fired after 3 sec from injection, i.e. after the gas had reached thermal equilibrium with the tube. The trend shows that, for temperatures above 150 °C the transition distance increases from about 30 cm at room temperature, to more than 60 cm.

2)Determination of the delay of onset of cool flame with respect to tube temperature.

Before testing the effect of cool flame on transition distance to DDT, it was necessary to predict in advance the instant of onset of cool flame. It was observed that at relatively low temperature, i.e. close to the lower temperature limit, time of onset of cool flames was rather inconsistent, and differences up to 3 sec were obtained. In fact, cool flames appeared randomly at different locations along the tube with a well defined front that would oscillate slowly back and forth along the tube up to three times. By increasing the temperature of the tube, the delay time for onset of cool flame became shorter and very reproducible. Also cool flame appeared as a single luminous starting region at the far end of the tube propagating back toward the inlet until the whole tube was glowing of a very fainted blue light. The thermocouple indicated that this phenomenon would last for 3 or 4 sec. More sensitive thermocouples (25 μm diameter) never detected temperature increases over 130°C at the appearance of cool flame. Given that for temperatures above 360 °C the time of onset of cool flame was very reproducible, to increase the accuracy in measuring the delay time, an electret microphone was installed in substitution of the pressure transducer. Figure 3 shows the comparison between the microphone signal and the thermocouple trace at the onset of a cool flame. This test proved that the thermocouple was sufficiently accurate to determine the time of onset of cool flame. Figure 4 shows the trend of time of onset of cool flame with respect to tube temperature at two different temperatures of the pre-heater. The graph points out that the effect of increase of tube temperature tends to determine a time of onset of cool flame of about 0.4 sec. Below this value the temperature and pressure reading were influenced by the effect of the injection of the gas and the time of onset of cool flame could not be evaluated. However from “visual inspection” at temperatures above 480 °C it seemed that cool flame appeared at the inlet at the instant of injection.

3)Verification of the effect of cool flame on transition distance to DDT.

The effect of cool flame on the pre-detonation distance was investigated at three different tube temperatures maintaining the pre-heater at 300 °C. From the results of the preliminary tests, when the detonation tube was at 360 °C, onset of cool flame occurred with a delay time of 820 ms from the instant of opening of the solenoid valve. For a tube temperature of 380 °C and 400 °C onset of cool flame was

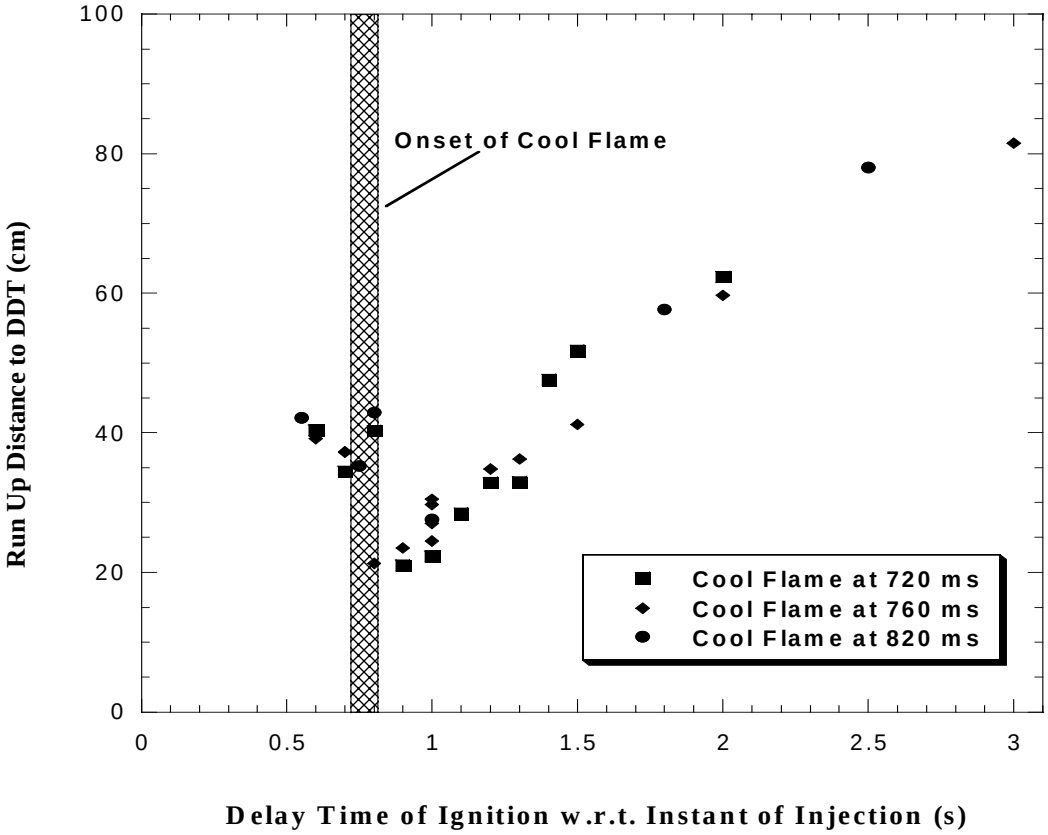

Fig. 5 Run up distance to DDT as function of ignition delay.

observed with delay times of 760 and 720 ms respectively with a resolution of 10 ms. Considering that the time necessary to fill the tube was about 500 ms, a series of shots were fired varying the time of ignition, from 0.5 to 3 second with respect to the instant of opening the solenoid valve. This time interval covered the entire region before and after onset of cool flame. The overall results are reported on Figure 5 and point out the general trend of a reduction of transition distance to DDT of about 20 cm (50%) when the mixture is spark ignited within 100 ms from the onset of cool flame.

Discussion and Conclusion

Run up distance for transition from deflagration to detonation turned out to be dependent on the temperature of the gas. In particular the transition distance increased for temperatures above 200 °C and it doubled for temperatures above 250 °C. This tendency drastically changed when the gas was in the cool flame region. A significant reduction in transition distance to DDT from 40 cm down to 20 cm was measured when the flame was ignited about 100 ms after onset of cool flame.

It is important to underline that, while onset of cool flame always started at the far end of the tube and propagated back to the inlet, the mixture was ignited from the side of the inlet. Therefore, when the mixture was ignited within 100 ms from onset of cool flame, the first part of the acceleration of the flame occurred in a mixture which had not undergone cool flame oxidation, but it was on the verge to onset such process. These were the conditions of the mixture for which the maximum sensitizing effect was detected.

The results show that for temperatures below 280-290 °C cool flames never appeared, indicating that the chemistry responsible for the appearance of cool flames, is promoted only above a critical temperature. The reduction of run up distance observed in the cool flame region demonstrated the presence of free

radicals that are not present in the mixture at lower temperatures, for this reason they must be the same as those responsible for the appearance of cool flame. These free radicals however do not have a long life time as demonstrated by Figure 5 that shows how the sensitizing effect of cool flame vanishes when the mixture is spark ignited more than 0.3 sec after onset of cool flame. These results confirm the prediction of Sokolik that the cool flame oxidation does have a sensitizing effect on the run up distance to DDT. Cool flame oxidation occurs when the concentration peroxides reaches the maximum, however this concentration falls when the cool flame is formed.

References

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