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Detonation Sensitization of Hydrocarbon Fuels via Peroxide Addition

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### Introduction

There is considerable interest in techniques to promote the reaction rate of hydrocarbon fuels for highspeed airbreathing applications such as scramjets and pulse detonation engines (PDE's). In order to increase the sensitivity to detonation initiation for PDE's, a number of chemical additives have been investigated in recent years. The use of nitrates (e.g., isopropyl nitrate, ethylhexyl nitrate) has been recently studied by Davidson et al. [1], Sidhu et al. [2], Zhang et al. [3], and Hitch [4]. The effect of nitrates on reducing run-up distance to detonation and detonation cell size has been small. The study by Zhang et al. [3], for example, found that cell size of hexane varied linearly with the addition of IPN, such that a reduction in cell size of 50% required roughly equal amounts of hexane and IPN. The recent study by Pinard et al. [5] suggests that the proposed mechanism of nitrate sensitization, i.e., the generation of  $NO_2$  by decomposition of the nitrate, has no sensitizing effect whatsoever, as the direct addition of  $NO_2$  to propane had no observable effect on cell size or run up distance.

A more promising result is the "cool flame" sensitization effect, as first discovered by Shchelkin and Sokolik [6], and recently reproduced by Romano et al. [7] The partial oxidation of a hydrocarbon/oxygen mixture via a cool flame was seen to result in a reduction of the run up distance by approximately 50%. A chemical kinetic simulation of the cool flame reaction was performed in order to identify the mechanism responsible for the observed effect. By simulating the cool flame kinetics, and then "freezing" the chemistry in order to perform a calculation of the detonation length, the variation of detonation cell size through the cool flame process could be predicted, in good agreement with the experimentally observed cell size.[8] A sensitivity analysis was performed to identify the mechanism of sensitization during the cool flame. Although no single ingredient was identified, the combination of hydroperoxides generated by the cool flame and the elevated temperatures during the cool flame were suggested as a possible mechanism. [8] This suggests that the same sensitization effect may be reproduced outside of the relatively narrow range of pressure and temperature in which cool flames are observed if the same hydroperoxides can be artificially introduced.

The use of peroxides (hydrogen peroxide in particular) as a means to sensitize a hydrocarbon fuel has been proposed by others. Frolov et al. [9] and Catoire et al. [10] have recently proposed blending

hydrogen peroxide  $(H_2O_2)$  with hydrocarbon fuels in order to increase their detonation sensitivity. In independent studies using chemical kinetic models of hydrocarbon combustion, they have shown that a significant reduction in detonation cell size is possible by a small amount of peroxide addition to the hydrocarbon fuel.

The present study will experimentally examine the effect of adding a hydroperoxide (*tert*-butyl hydroperoxide) to a hydrocarbon fuel (decane). This peroxide was selected due to its similarity to the hydroperoxides that appear during the cool flame process. The fuel and hydroperoxide are mixed prior to the preparation of a fuel/oxygen mixture, which is then injected into a heated detonation tube ( $T_{tube} = 150 - 200 \text{ °C}$ ). The sensitivity of the resultant mixture will be quantified by measuring the run-up distance to detonation and comparing the results to those obtained with pure decane.

### **Experimental Apparatus**

These experiments are performed in a heated glass detonation chamber (5.12 cm inside diameter and 1.23 m long). A schematic of the experiment is shown in Fig. 1. The use of a glass tube facilitates observation of the combustion and detonation phenomena, and also helps prevent undesirable catalytic



Fig. 1 Schematic of experimental set-up used to investigate the effect of peroxides on DDT in hydrocarbon fuels.

and contamination effects that have been observed with steel chambers. The tube is heated in order for the vapor pressure of the hydrocarbon fuel to be sufficient to provide the required partial pressure of the mixture. In addition, the cool flame sensitization effect, as described in the introduction, is also expected to require elevated temperature. The tube is fitted with a Shchelkin spiral that is 4 mm in diameter, with a pitch of one turn per tube diameter. The Shchelkin spiral is to ensure a reproducible run-up distance to detonation that depends upon the turbulent flame acceleration phase, rather than the laminar to turbulent flame transition.

The fuel rich mixture ( $\phi = 1.2$ ) of decane/oxygen is prepared via the method of partial pressures in a heated mixing chamber. The fuel used is decane. The peroxide used in the study is *tert*-butyl hydroperoxide (tbhp: (CH<sub>3</sub>)<sub>3</sub>COOH, MW: 90.12). This peroxide is available from Aldrich in a variety of

forms, including a 5.0-6.0*M* solution in decane. This makes using decane as the candidate fuel particularly attractive: pure decane can be blended with the tbhp/decane solution in order to control the peroxide concentration in the fuel. The fuel is vaporized and mixed with oxygen in the mixing chamber for several minutes to ensure a homogenous mixture.

The mixture is injected into the detonation through a pebble-bed heater that is the same temperature as the tube. The pebble bed consists of a stainless steel cylinder filled with steel spheres in order to increase the

surface area and bring the mixture to the desired temperature quickly. After injection into the detonation tube, the mixture is allowed to equilibrate in the tube for a few seconds, then spark-ignited at one end. The initial pressure for all tests was 10 kPa. The propagation of the flame is monitored via photodiodes that observe the combustion wave via fiber optics mounted on the tube surface.



Fig. 2 Comparison of decane (with various concentrations of tbhp) to pure decane at 150 °C, 10 kPa.

### **Results**

The averaged result of 12 experiments in pure decane at 150 °C and 10 kPa initial pressure is shown in Fig. 2 as a plot of the combustion wave velocity as a function of distance along the tube. The Chapman Jouguet (CJ) detonation velocity is denoted as a dashed line. The combustion wave consistently transitioned to a detonation at a distance of 50 - 60 cm from the ignition point. The results with 6 wt%, 15 wt%, and 30 wt% tbhp addition to the decane fuel are also shown. The transition to detonation in this case consistently occurs in the range 35 - 40 cm from the ignition point, a significant reduction in run up distance to detonation. The sensitization effect appears to be nearly independent of the concentration of tbhp. A lower bound on the concentration of tbhp necessary for this effect has yet to be established.

If the tube temperature is increased to 200 °C, the effect on run up distance becomes more pronounced. Here, averages of approximately 12 shots for each mixture composition (6, 15, and 30 wt% of tbhp in decane) are shown. The run up distance to detonation decreases from 60 cm to 25 - 30 cm with the addition of the peroxide, a reduction of more than 50%. Again, the effect does not appear to be particularly sensitive to the amount of peroxide added, although the greatest concentration did result in the shortest run up distance.

# Conclusions

The addition of relatively small concentrations of *tert*-butyl hydroperoxide is seen to have a significant sensitizing effect on the detonation sensitivity of decane/oxygen mixtures at elevated temperature. The magnitude of the reduction in run-up distance (approximately 50%) is comparable to the effect observed in the "cool flame" sensitization experiment of Romano et al. [7], although the mechanism of sensitization has not been proven to be the same in both cases. We may speculate that rapid generation of OH radicals by decomposition of the peroxide may provide an effective "jump-start" to the chain initiation and branching reactions that govern the induction length kinetics, which in turn control detonation sensitivity. The fact that relatively small concentrations (~6 %) of sensitizer are necessary to realize this effect suggests that hydroperoxides warrant further investigation as sensitizers for hydrocarbon fuels.

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