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Sensitization of Hydrocarbon-Oxygen Mixtures to Detonation Via Cool Flame Oxidation

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Abstract

The effect of cool flame partial oxidation on the detonation sensitivity of hydrocarbons was experimentally investigated. Sensitivity to detonation was quantified by measuring the detonation cell-size using the smoked-foil technique. A rich pentane oxygen mixture was preheated in a pebble bed before filling a heated glass detonation tube to sub-atmospheric pressure. Cool flame reaction, monitored by a thin K-type thermocouple, occurred in the detonation tube after a known time interval as determined by the tube temperature. The mixture was ignited by a weak spark and onset of detonation was monitored using a streak camera. A smoked foil was inserted in the far end of the tube (opposite to ignition) to permit the measurement of the cell size of a well-developed detonation. The results show that the cell pattern becomes very regular at high temperature but the average cell size practically does not change. However, when the mixture was detonated while undergoing the cool flame reaction, a significant reduction of the cell-size was obtained (as large as 50%). The sensitizing effect was found to occur only in the initial stage of the cool flame reaction. When the mixture was ignited a few hundreds of milliseconds after the beginning of the cool flame, the mixture was desensitized and the cell size increased.

The explanation of the sensitizing effect of the cool flame reaction was investigated by using a chemical kinetic model to simulate the cool flame reaction and identify the chemical species that may be responsible for the observed results. By taking snapshots of these chemical concentrations during the simulated cool flame, these species were used as reactants in a zero-dimensional code to compute the induction kinetics for a Chapman Jouguet detonation. The numerically computed induction times closely follow the experimentally observed cell sizes and confirm that the sensitizing effect of the cool flame reaction may be attributed to the presence of free radicals and peroxides associated with the beginning of the cool flame process. However, these radicals are consumed as the cool flame reaction proceeds and the mixture becomes insensitive again.

Introduction

From a chemical kinetic point of view it is known that free radicals enhance the detonation sensitivity of combustible mixtures by reducing the induction time. In a series of pioneering experiments, Shchelkin and Sokolik [1] reported a reduction of the run-up distance to detonation (DDT) of a pentane-oxygen mixture when it was spark ignited in the "cool flame region." Their conclusion was that relatively long-lived peroxides and free radicals were responsible for these results. Recently, Romano *et al.* [2] have confirmed Sokolik's early results and demonstrated that a reduction of about 50% in the run-up distance can be obtained when a pentane-oxygen mixture is spark ignited while it uniformly undergoes the cool flame partial oxidation process. However, care must be taken in using the run-up distance to detonation as a measure of the detonation sensitivity of a combustible mixture since it can at best provide only a qualitative measure of the detonation sensitivity. The run-up distance to DDT is not independent on the fluid dynamics involved during the acceleration of the flame, and involves the transition between different mechanisms of combustion wave propagation, which may not depend on the induction kinetics of the mixture. Detonation sensitivity is best measured experimentally by parameters such as the detonation cell size [3]. Therefore, the objective of the present study is to experimentally measure the detonation sensitivity of an n-pentane-oxygen mixture while it is undergoing the cool flame oxidation process by measuring the detonation cell size. A complimentary theoretical study based on a model of pentane combustion [4] is also used to numerically simulate the experimental results of the investigation to provide a better understanding of the exact mechanism responsible for the sensitization.

Experimental Apparatus and Procedure

The experimental apparatus is illustrated in Fig.1, and described in detail in a previous work [2]. In order to achieve a well-controlled and reproducible experiment, a pebble bed pre-heater was used to uniformly heat up the mixture to a temperature below the cool flame region. The uniformly preheated mixture was then injected in the evacuated heated detonation tube, where it underwent the cool flame process.

All experiments were conducted at constant mixture composition (ϕ = 1.1) and density (ρ = 170 Kg/m^3 ± 5%), while varying the instant of ignition by using a delay generator. In this manner the mixture was spark ignited at different times with respect to the instant of the onset of the cool flame. Initiation of detonation was observed with the use of a streak camera, and the detonation sensitivity was measured using the smoked-foil technique. The smoked foils were 0.005 inch thick, 50 mm wide and 300 mm long and located at the opposite end of the tube from the igniter. They were rolled lengthwise and carefully inserted in the detonation tube. The temperature range chosen for this study was 375-380 °C, where the expected delay time for the onset of cool flame was just below one second after the injection of the mixture into the heated detonation tube from the pre-heater [2].

Experimental Results

Experiments were first carried out to determine the effect of temperature alone on the detonation cell size without cool flame reaction. The detonation cell pattern (for n-pentane-oxygen mixture at equivalence ratio ϕ = 1.1 and pressure of 25 kPa) at about 360 °C was found to be very regular with an average cell size of 5-6 mm while the detonation cell pattern at room temperature for the same density of the mixture was found to be irregular but with an identical average cell size (Fig. 2). The detonation cell size measurements provide clear evidence that the effect of temperature, in the range 300-600 K, does not decreases the cell size and it does not alter the detonation sensitivity of the mixture, provided the density of the mixture remains constant [5, 6].

When the mixture was detonated at the beginning of the cool flame oxidation, a significant reduction of the detonation cell size was observed. The average dimension was found to be 2-3 mm, compared to 5-6 mm obtained by detonating the mixture before the starting of the cool flame. If the mixture was ignited after a long delay time, however, when the cool flame reaction had completed, the cell size returned to the original value or sometimes was even larger (Fig. 2). This increase in cell size after a long delay indicates a desensitizing effect in the mixture. The results are summarized in Fig. 3, which shows the variation of cell size as a function of the delay time between mixture injection and ignition. The shaded area indicates the time interval during which the cool flame reaction occurred.

Numerical Simulation

The reaction mechanism used for this study has successfully been applied previously by Ribaucour *et al.* [7] for modeling experimental data on auto-ignition of the three isomers of pentane in a rapid compression machine. In the present numerical study, a constant volume, static reactor was considered with n-pentane as the fuel at an equivalence ratio of $\phi = 1.1$, an initial temperature of 320 °C, and an initial pressure of 25 kPa. A heat transfer model was used, assuming a reactor wall temperature of 320 °C and a characteristic heat transfer time of 0.1 sec.

Under these conditions, three distinct cool flames were observed in the computed results, until fuel consumption precluded further cool flame activity. Multiple cool flames are common in fuel/oxygen mixtures under similar conditions [8]. The results of the cool flame simulation are summarized in Fig. 4, showing the temperature and concentrations of n-pentane, HO_2 and H_2O_2. The overall duration of the cool flame was approximately 0.5 seconds, and each of the three cool flames is noted by a step decrease in pentane, a step increase in H_2O_2, and spikes in temperature and HO_2 concentration. Other radical species such as OH and many of the alkylperoxy radicals had concentration profiles similar to that shown for HO_2 in Fig. 4. The overall fuel consumption in the cool flame period is approximately 67%, from 0.12 to 0.4 mole fraction. The fuel decrease, the HO_2 levels, and the temperature spikes all indicate that the first cool flame was somewhat more vigorous than the second or third. None of the cool flames reaches the temperature at which the H_2O_2 decomposes, so a true ignition event is not observed [4].

Beginning with the completely unreacted mixture at 0.6 seconds in Fig. 4 until the conditions following the end of the cool flame at 1.2 seconds, a series of "snapshots" were taken of the chemical compositions at different instants during the cool flame simulation in Fig. 4. For each instant, post-shock induction time calculations were executed using the CJ conditions to define the shock speed, assuming that the reactive system is "frozen" during the passage of the shock wave. From the computed induction times, cell sizes were calculated at each point, assuming that the cell size was 50 times the induction length, similar to results observed for fuel/oxygen mixtures in previous kinetic modeling studies [9].

The results of the simulation were remarkably similar to the experimental data as shown in Fig. 5. The time of the first cool flame temperature peak ($T > 900$K) is at 0.769 seconds. At 0.6 seconds the cell size is 2.7 mm and remains constant until dropping at 0.768 seconds to 1.7 mm and falling to a minimum of 1.5 mm at 0.769 seconds when the cool flame temperature reaches its highest value. Only 300 ms after the beginning of the simulated cool flame, the calculated cell size is 3.3 mm, reflecting the same de-sensitizing effect observed during the experiments.

A series of sensitivity analysis calculations was performed to try to isolate the features of the cool flame responsible for the computed reductions in cell size. One at a time, specific species concentrations during the cool flame were varied to see if any of them could produce the type of variations in computed cell sizes seen here. However, these sensitivity studies indicated that no single species from the cool flame could be found responsible for the observations, and while the three temperature peaks during the cool flame produced somewhat reduced cell sizes, the cell size total reductions could not be attributed only to these temperatures. As shown in (Fig. 6), if the mixture composition immediately prior to the cool flame reaction ($t = 0.6$ s) is brought to the same temperature and pressure that exists at the cool flame peak, a significant reduction in cell size occurs. Likewise, if the composition at the cool flame peak ($t = 0.769$ s) is frozen and brought to the same temperature and pressure as the initial mixture prior to reaction, the increase in mixture sensitivity is nearly the same. Thus, while both radical concentration and temperature have an influence on the detonation sensitivity, their combined effect is responsible for the observed decrease in induction time. The only way to produce the computed cell size results was to combine the effects of enhanced radical concentrations and higher temperatures, as indicated in Fig. 6.

Discussion and Conclusion

Experiments were carried out to examine the effect of “cool flame” pre-oxidation of a hydrocarbon-oxygen mixture on the detonation sensitivity of a pentane-oxygen mixture. During the experiment, the mixtures were first heated up rapidly to initiate a cool flame, then, at different stages during this process, the mixtures were detonated, and the detonation cell size was measured using the smoke foil technique.

The kinetic model employed in this work captured the most important features of the phenomena encountered. The simulated temperature profiles of the cool flames were very similar to the experimental traces obtained with the use of thermocouples [2] although the computed temperature peaks were 200 °C higher than the experimentally measured cool flames. The kinetic model showed the following reaction sequence: addition of pentyl radicals to O_2 to form pentyl peroxy, pentyl peroxy isomerization, and subsequent reaction with O_2 leading to chain branching. This process is typical of the first stage ignition mechanism (cool flame chain branching) and ends when the increased temperature reverses the addition reaction of alkyl radicals to molecular oxygen. This negative temperature coefficient of oxidation shuts off the main chain branching reaction pathway and halts the ignition. Computed induction times and cell sizes qualitatively reproduced the experimental observations without extrapolating from any data point by assuming that the cell size was approximately 50 times the induction time.

In relating the computed kinetic results to the experimental observations, it is essential to remember that the computations describe a single, idealized spatial point, and there is no consideration of variations in composition or temperature in the reactive medium. Even if the assumption is accurate that spatial species transport is unimportant, heat transfer to the walls of the detonation tube produces a non-uniform temperature field that will affect the observations. These non-uniformities will in effect smear out the results of Fig. 5 over the reactive mixture in the tube, so that although at each location the mixture may be passing through the cool flame of Fig. 4, not all of the reactive mixture locations will be exactly in phase with each other. This helps explain why the three cool flames were not observed in the experiments, since they are occurring and not occurring throughout the combustion chamber over a period of time. The same argument shows that the most sensitive mixture conditions in the first cool flame will also be occurring at a range of times in the reactive mixture, so that sensitization will persist for a longer time than that computed by the idealized kinetic model.

As noted above, the modeling analysis did not indicate that any specific species in the cool flame is alone responsible for the observed sensitization. Instead, the combination of elevated temperature and radical levels in each cool flame provides the shorter induction time and smaller cell size. Although the kinetic modeling indicates these peaks occur at only a few locations in the cool flame region, spatial non-uniformities in the experiments can distribute these cool flame reactive peaks within the reactive mixture over a time interval that is somewhat longer than in the idealized computed results would indicate, effectively diffusing the sharp cool flame peaks into a broad range that is still sensitized overall.

The kinetic model also shows why the effect of the cool flame first sensitizes the reactive mixture and then in effect desensitizes it. The considerable amount of fuel consumption that occurs from the series of cool flames means that the post cool flame mixture has much less exothermicity associated with it than the initially unreacted mixture, and the resulting larger cell sizes are the product of the different CJ conditions in the partially reacted gases.

While the numerical simulation was able to explain the kinetic mechanism of the cool flame reaction indicating the global effect of temperature and active free radical concentrations, the experimental results conclusively demonstrate that the cool flame phenomenon can lead to a significant increase of the detonation sensitivity of heavy hydrocarbon mixtures.

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Figure captions

Figure 1: Experimental set-up.

Figure 2: Samples of smoked foils.

Figure 3: Effect of cool flame on detonation cell size in n-pentane-oxygen ($\phi = 1.1$) at constant density ($\rho = 170 Kg/m^3 \pm 5\%$).

Figure 4: Simulated temperature history of cool flame reaction and chemical concentration profiles.

Figure 5: Simulation of effect of cool flame on detonation cell size in n-pentane-oxygen.

Figure 6: Sensitivity analysis calculations.

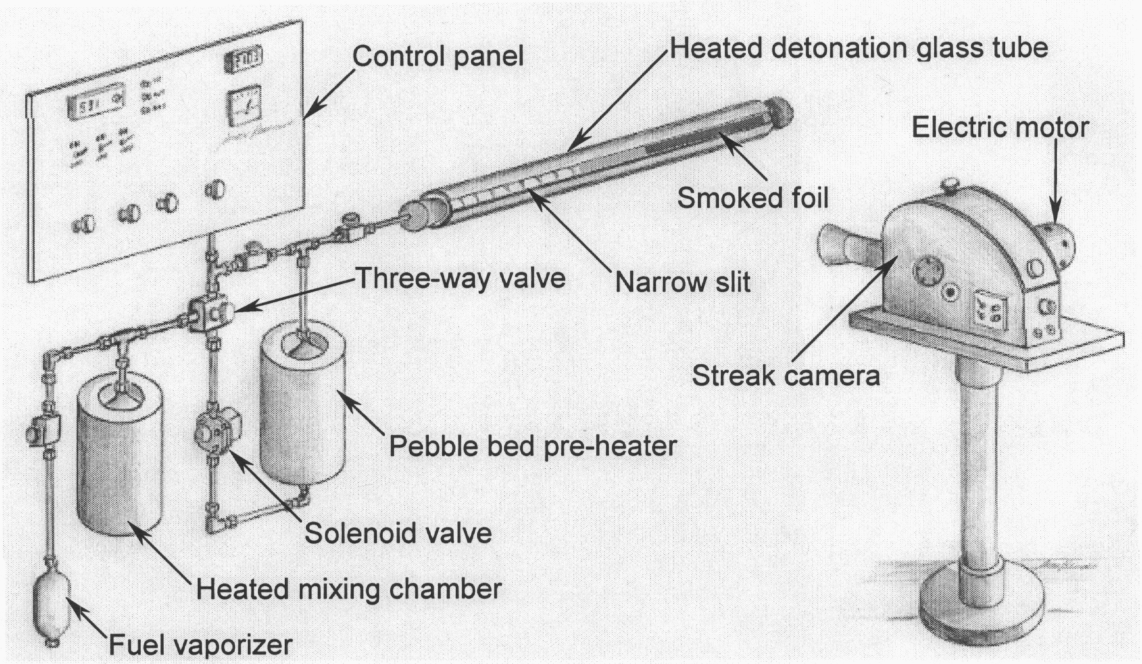

Control panel
Heated detonation glass tube
Electric motor
Smoked foil
Three-way valve
Narrow slit
Streak camera
Pebble bed pre-heater
Solenoid valve
Heated mixing chamber
Fuel vaporizer

Figure 1

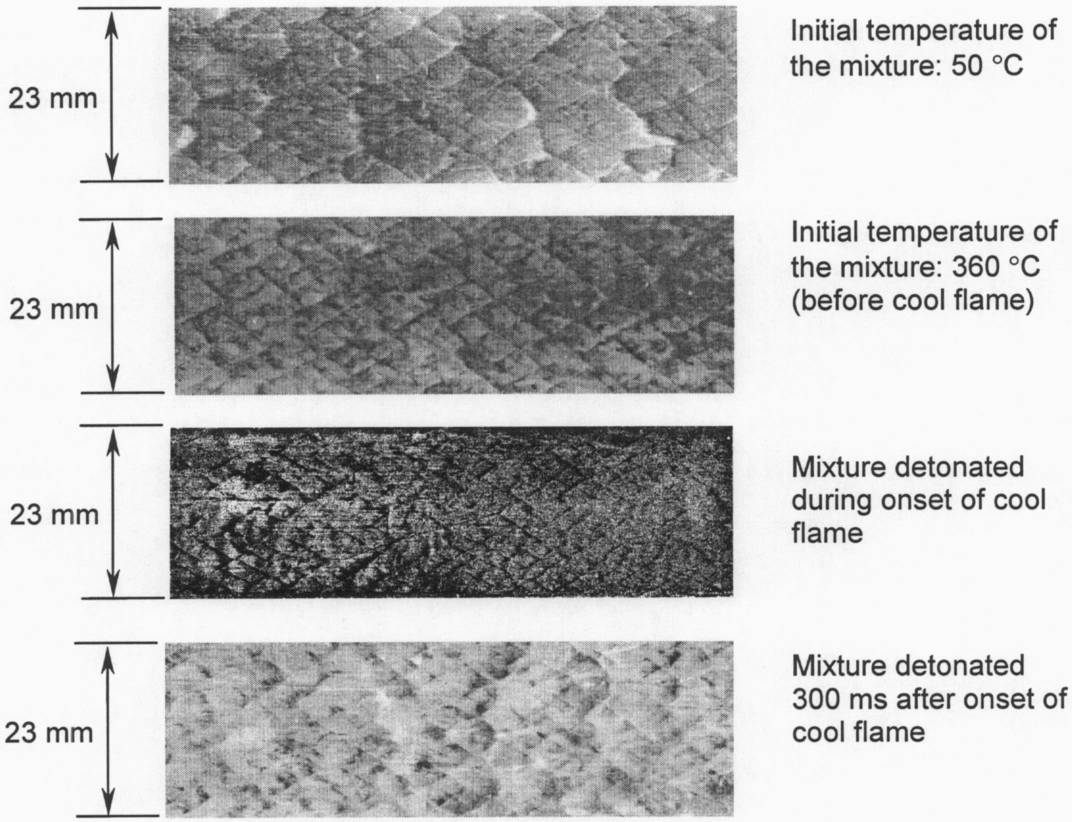

23 mm
Initial temperature of the mixture: 50 °C
23 mm
Initial temperature of the mixture: 360 °C (before cool flame)
23 mm
Mixture detonated during onset of cool flame
23 mm
Mixture detonated 300 ms after onset of cool flame

Figure 2

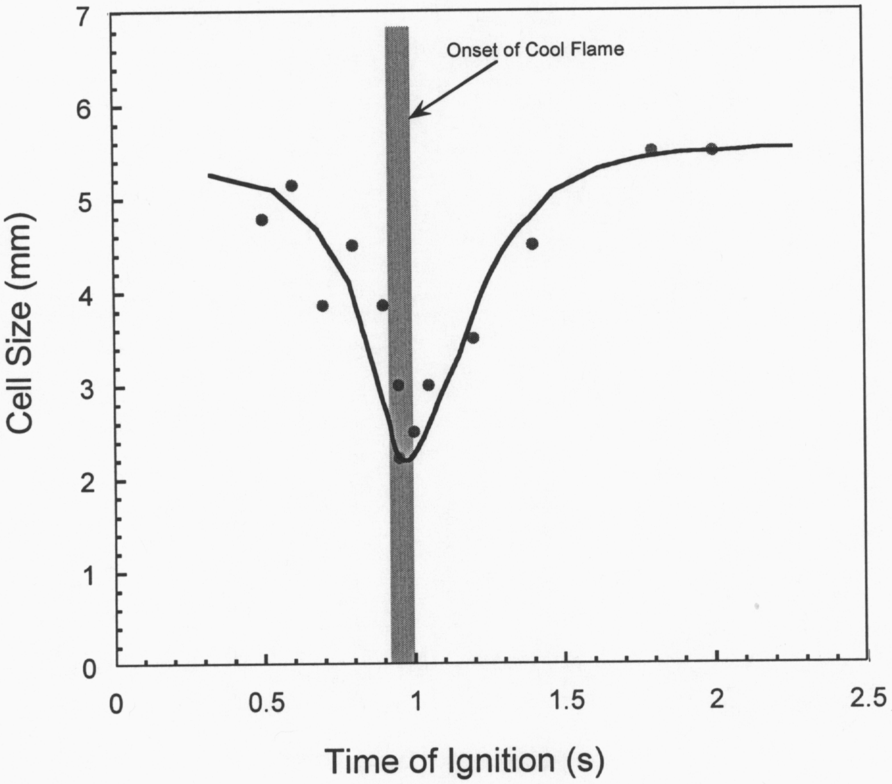

Onset of Cool Flame
Cell Size (mm)
Time of Ignition (s)
0
1
2
3
4
5
6
7
0
0.5
1
1.5
2
2.5

Figure 3

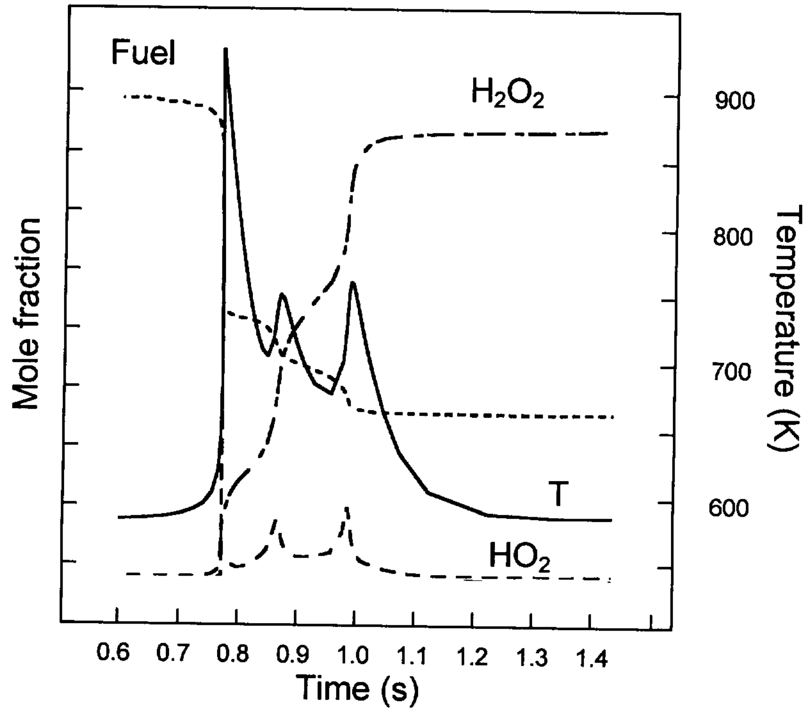
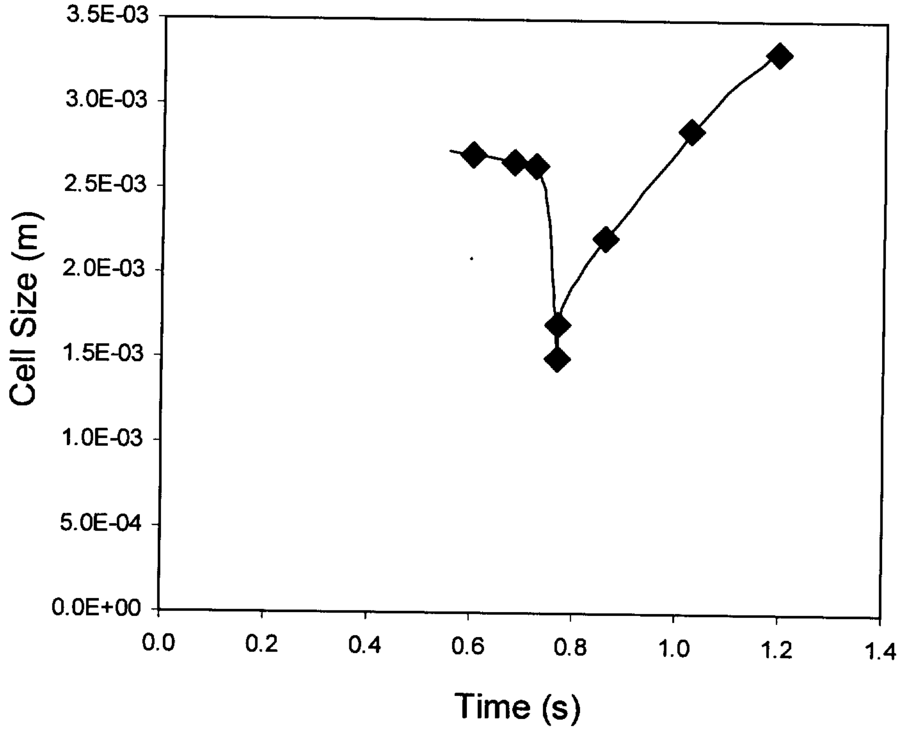

Fuel
H_2O_2
T
HO_2
Mole fraction
Temperature (K)
900
800
700
600
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
Time (s)

Figure 4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3.0E-03
2.5E-03
2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
Cell Size (m)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Time (s)

Figure 5

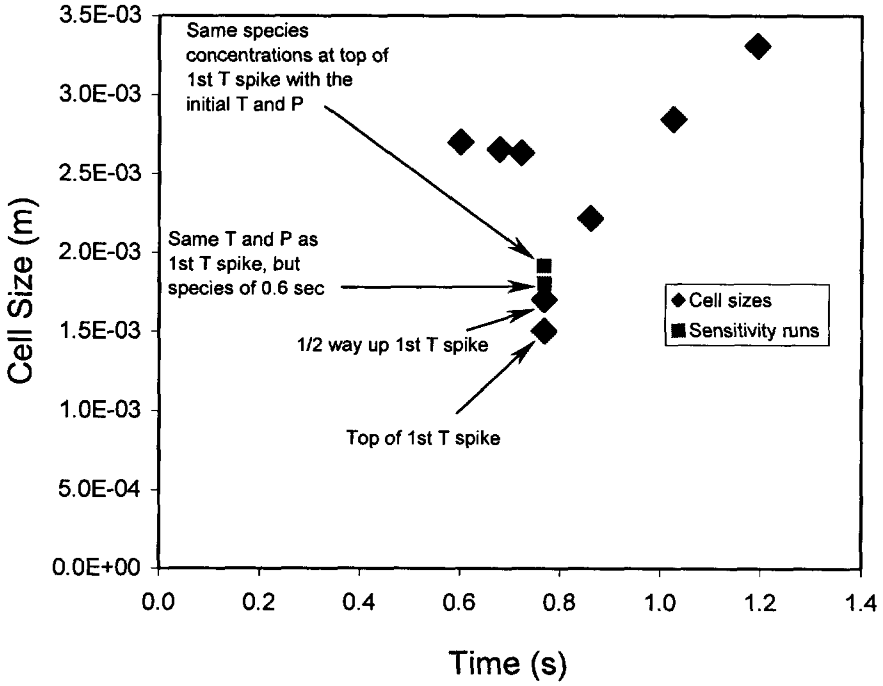
3.5E-03
3.0E-03
2.5E-03
2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
Cell Size (m)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Time (s)
Same species concentrations at top of 1st T spike with the initial T and P
Same T and P as 1st T spike, but species of 0.6 sec
1/2 way up 1st T spike
Top of 1st T spike
◆ Cell sizes
■ Sensitivity runs

Figure 6