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# The Role of Surface Generated Radicals in Catalytic Combustion

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## RESEARCH OBJECTIVES

Numerous studies of the feasibility of applying catalytic combustion to practical combustion systems have been made in recent years. This work has been motivated by the potential advantages of high temperature catalytically assisted combustion over conventional combustion. These studies include the development of catalytic combustors for aircraft gas turbines [1-6], stationary gas turbines [7-12], highway vehicle gas turbines [13-17] and boilers [11]. Other studies have focused on catalytic combustion of particular fuels such as methane [18-20], low-BTU gases [9,21], No. 6 oil [22], heavy fuels [23] and coal derived liquids [24]. The potential for low conversion of fuel-bound nitrogen to $NO_x$ has also been investigated [22,25-29]. The advantages of catalytic combustion which have been demonstrated by such studies include lower emissions, higher efficiency, increased operational stability, stable operation at lower equivalence ratios, improved pattern factor and wider fuel specifications. Still other work has been concerned with catalyst durability [30,31] and with the development of mathematical models which can be used to interpret experimental data and for combustor design optimization [32-37].

Under typical catalytic combustion operating conditions there are a number of physical and chemical processes which are important in terms of the catalytic combustor performance [38-40]. These include axial and radial convection of species, heat and momentum; axial and radial diffusion of species, heat and momentum; axial heat transfer in the substrate by conduction and radiation; gas phase chemical reactions and surface chemical reactions. The overall conversion efficiency of a catalytic combustor under normal operating conditions is typically mass transfer limited, with most of the fuel being consumed near the channel entrance by surface reactions and the remaining fuel being consumed near the channel exit by gas phase reactions.

Specific studies have been made to elucidate the roles of the various physical and chemical processes which effect catalytic combustion. For example, Marteney and Kesten [41] diluted the reacting mixture with argon, thereby limiting the temperature rise and making the surface reactions dominant. Bruno et al. [42] ran with $CO/O_2$/inert mixtures and by changing the inert ($N_2$, A, He and $CO_2$ were used) the diffusion characteristics of the flow field were varied. Hiam et al. [43] and Schwartz et al. [44] have measured the heterogeneous ignition temperatures as indicated by exothermic surface reactions on platinum and palladium filaments exposed to flows of various hydrocarbon-oxygen mixtures. Ablow et al. [45] theoretically and experimentally studied the relative importance of gas phase and surface reactions for the case of catalytic combustion in a stagnation point boundary layer, the advantage being that such a flow field is well understood thus simplifying the formulation of the mathematical model which was used to interpret the experimental results.

The objective of this research was to improve our understanding of the role of catalytic surface reactions in determining the performance characteristics of practical catalytic combustors. It is generally acknowledged that under typical fuel lean operating conditions, fuel and oxygen react on the surface to form water and carbon dioxide and that the resultant heat release and fuel consumption act to enhance and inhibit, respectively, the downstream gas phase and surface reactions. Since the competition between these two processes is very important in determining the gas phase ignition characteristics for flow over a catalytic surface [46], part one of this research was to experimentally characterize the ignition of lean propane/air mixtures over a platinum catalyst. Although there had been several theoretical studies of this process [33, 35, 46-48], prior to this work there had been no experimental studies. The experiments conducted in this study consisted of measurements of the catalyst substrate temperature profile and exhaust gas composition during the transient ignition process that follows the sudden turn on of the fuel.

The second part of this research was the investigation of the possibility that intermediate or radical species generated by the catalytic wall reactions can diffuse into the gas phase boundary layer and homogeneously catalyze the gas phase reactions. That such an effect may play a role in catalytic combustion is supported by low pressure studies of the oxidation of hydrogen on platinum where the production of OH was observed above catalyst temperatures of approximately 800°K [49-51]. It is also interesting that preliminary results using detailed kinetics for CO/air mixtures at atmospheric pressure indicate that $H_2O_2$ and $HO_2$, present in finite amounts in the same temperature range, are good candidates as species easily decomposed by platinum to form OH [52]. That significant OH production occurs at the catalytic wall under catalytic combustion conditions is also consistent with the experimental observations of Cattolica and Schefer [53,54] where they found net OH production in the boundary layer near the leading edge of a heated platinum plate in an $H_2$/air flow. Although the generation of radicals by catalytic processes and the effect on gas phase reactions has been previously observed [55], the importance of this phenomenon in catalytic combustion systems had not been previously studied. Such a phenomenon could be particularly important in determining the ignition temperatures, flammability limits, emission characteristics, sooting behavior and flame stabilization characteristics of practical catalytic combustors.

The second part of this research was an experimental study of the effect of surface generated OH radicals during the combustion of propane-air mixtures over platinum coated catalysts under catalytic combustion conditions. In particular, laser induced fluorescence was used to measure OH radical concentration immediately downstream of two catalytic plates in a stacked plate catalyst bed. It is important to realize that the effect of surface generated radicals should be evaluated under catalytic combustion conditions. This is because catalytic ignition, combustion and extinction involve the coupling of chemistry and fluid dynamics through the processes of gaseous convection and diffusion, substrate conduction and radiation, and gas and surface chemical reactions. It is the relative importance and the interaction of these phenomena which determine the overall performance characteristics such as ignition temperature or blowout limit, of a given catalyst-fuel system.

## STATUS OF THE RESEARCH

### Description of the Experiment

Both the transient measurement and the OH radical measurements were conducted in the same stacked plate catalytic combustor, which consisted of nine flat catalytic plates (100 mm long, 50 mm wide, 1 mm thick), spaced 6 mm apart. The catalyst plates (supplied by W. Retallick) were made from a steel alloy substrate, with an aluminum oxide barrier and an outer coating of platinum. Six 0.75 mm diameter holes were drilled into the side of the center plate at six axial locations and chromel-alumel thermocouples were inserted into these holes for measurements of the plate's axial temperature profile. A combination water cooled, gas sampling and thermcouple probe was used to obtain gas composition and temperature measurements at the exit of the catalyst bed. All experiments were with lean propane-air mixtures at one atmosphere pressure. In the transient experiments the inlet temperature and velocity were fixed, the fuel was turned on, and the transient response of the catalyst axial temperature profile and of the exhaust gas temperature and composition (i.e. carbon monoxide, carbon dioxide, propane, propylene, ethane, ethylene and methane) were measured at several axial locations along the length of the catalyst bed. The fuel transient, which was measured under cold flow conditions with a hot wire anemometer, was less than one second. The carbon monoxide and carbon dioxide measurements were made using non-dispersive infrared gas analyzers, which have a characteristic response time of less than five seconds. The hydrocarbon measurements were made using a multi-loop gas sample storage system with subsequent analysis by gas chromatography. The characteristic response time of the multi-loop gas sample system was less than ten seconds.

Optical access was available at several axial locations along the length of the catalyst bed through ten millimeter diameter windows located on opposite sides of the test section. Based on a similar experiment by Cattolica and Schefer [53,54], it was anticipated that the OH concentrations would be large enough for detection by resonance absorption spectroscopy. Under the conditions of our experiment the OH detection limit using the absorption technique was about $10^{16}$/cc, as compared to equilibrium OH concentrations of about $10^{13}$/cc (based on the overall equivalence ratio and the catalyst temperature). Measurements were attempted in the stacked plate combustor using resonance absorption and were unsuccessful, implying that the OH concentration was less than $10^{16}$/cc but still possibly greater than the overall equilibrium concentration. In order to extend the OH detection limits it was decided to use laser induced fluorescence (LIF). Because of the limited optical access with the stacked plate configuration, it was necessary to use "forward scatter" collection. The spatial resolution with this configuration is comparable to that of the absorption measurements, which is adequate for the two dimensional flow field between the catalyst plates. The main difficulty with this approach is in separating the fluorescence from the laser light. The optical configuration that has been successfully used is shown in Figure 1.

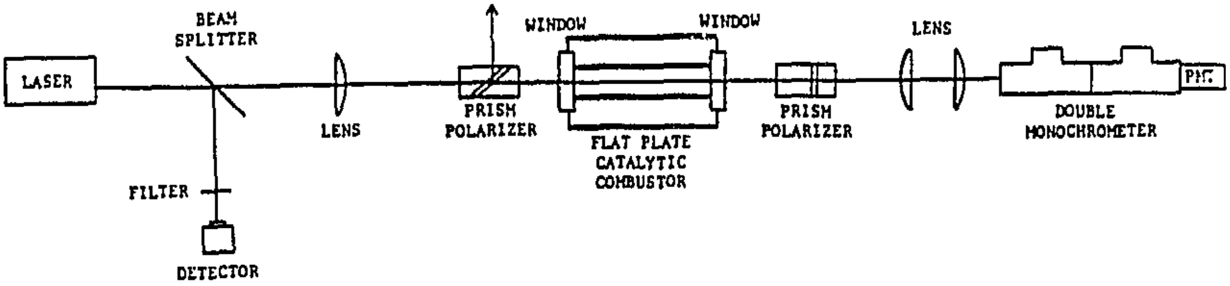

Figure 1. Laser Induced Fluorescence experimental configuration for catalytic combustion measurements.

The absorption transition is v = 0 to v = 1 at 2820 Å and the fluorescence from v = 1 to v = 0 at 3090 Å is detected. The use of polarization rejection and a 0.25 meter double monochrometer effectively blocks the laser light. The detection limit with the "forward scatter" LIF was approximately $10^{12}$/cc.

The laser used for the OH measurements was a Nd:YAG pumped dye laser which was frequency doubled to obtain the required ultraviolet wavelengths. The dye laser used a diffraction grating at grazing incidence. The resultant linewidth after frequency doubling was approximately 0.1 $cm^{-1}$. A typical OH excitation spectra obtained with this laser system and the "forward scatter" LIF in a methane-air flat flame burner is shown in Figure 2. The OH concentration measurements were made with the laser wavelength fixed on the $Q_1(2)$ line and a spectrometer slit function of 20Å.

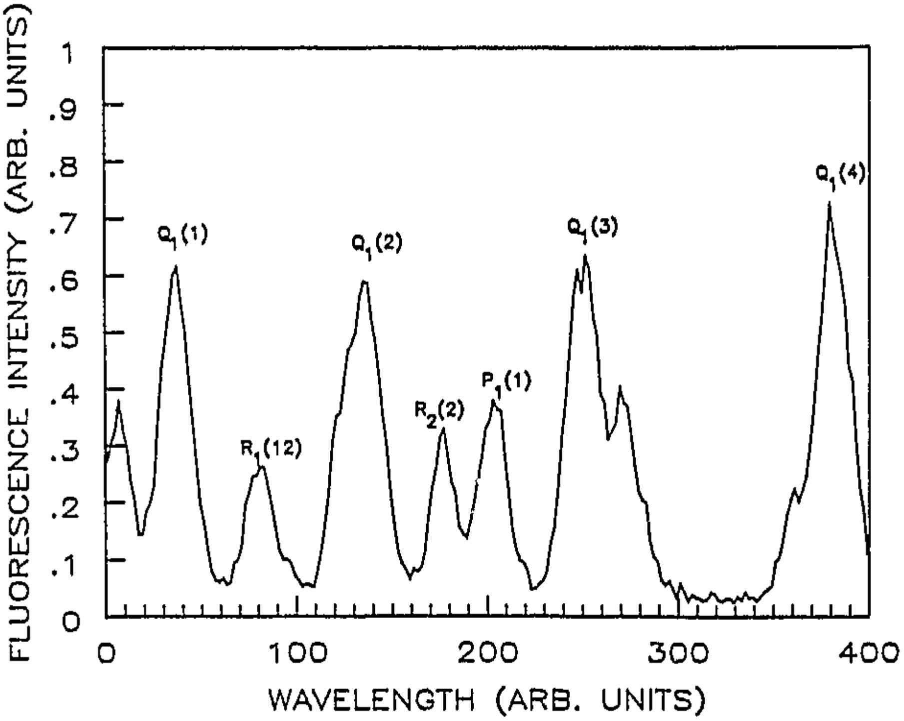

Figure 2. OH excitation spectra from methane-air flat flame.

Transient Measurement Results

The transient response of the substrate temperature profile is shown in Figures 3 and 4 where it can be seen that the front of the catalyst heats up first due to heat release by the catalytic surface reactions.

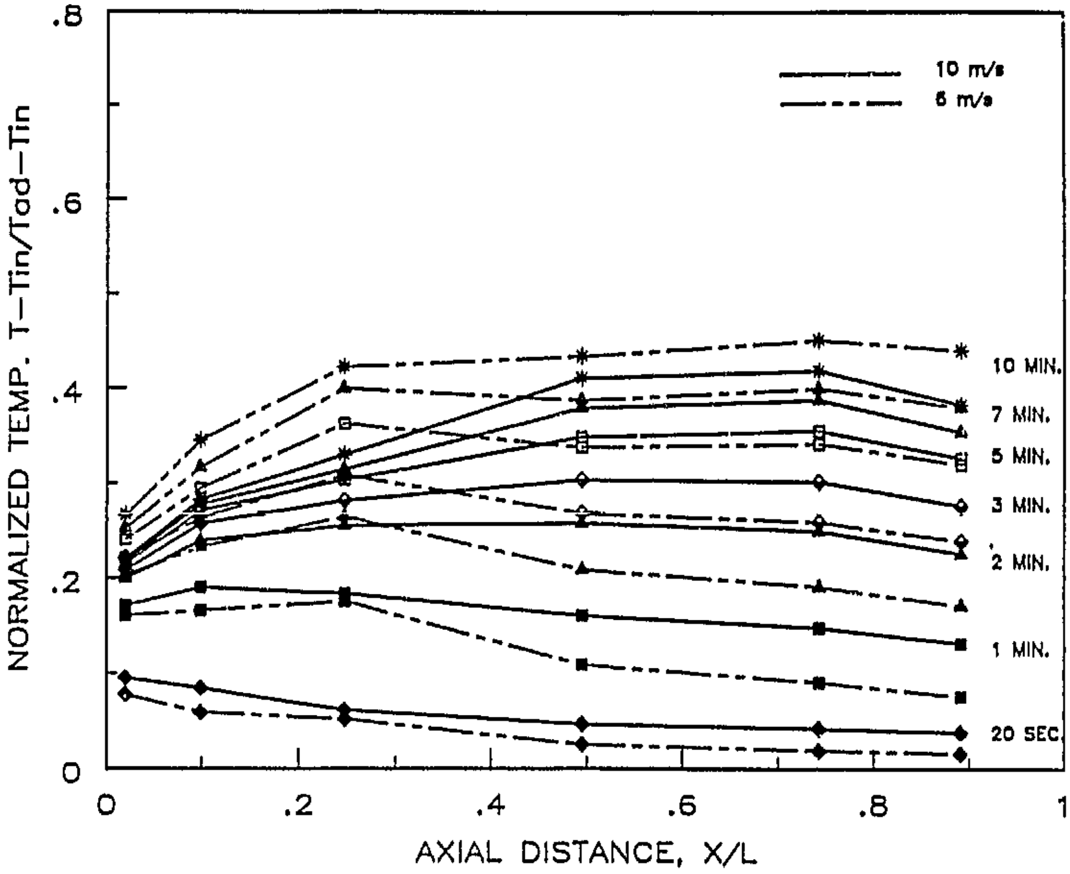

Figure 3. Substrate temperature profile transient: Inlet temperature = 700°K, propane/air equivalence ratio = 0.25.

These reactions however consume fuel and therefore the downstream sections of the catalyst are exposed to a lower equivalence ratio. The subsequent heat up of the back of the catlyst is strongly dependent on convective heat transfer from the front of the catalyst as can be seen by the fact that the back of the catalyst heats up more quickly when the reference velocity is

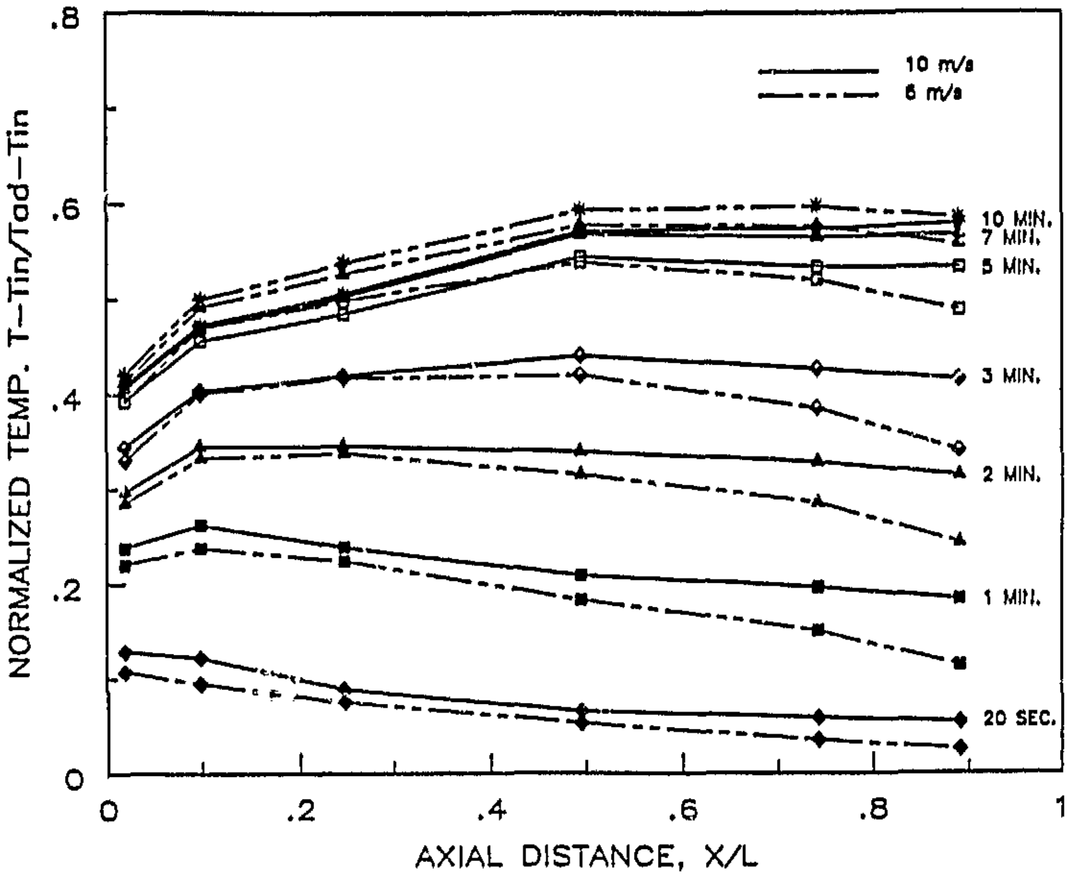

Figure 4. Substrate temperature profile transient: Inlet temperature = 700°K, propane/air equivalence ratio = 0.3.

increased from 6 m/s to 10 m/s. The steady state temperature profile appears to be relatively insensitive to a change in reference velocity from 6 m/s to 10 m/s when the equivalence ratio is 0.3. However, when the equivalence ratio is lowered to 0.25 this same change in reference velocity has a pronounced effect on the steady state substrate temperature profile.

The transient exhaust gas composition measurements for the 6 m/s reference velocity, 700°K inlet temperature, 0.3 equivalence ratio case are shown in Figures 5 and 6. These measurements were made 25 mm downstream of the catalyst bed exit. The $CO_2$ concentration (Figure 5) is found to increase

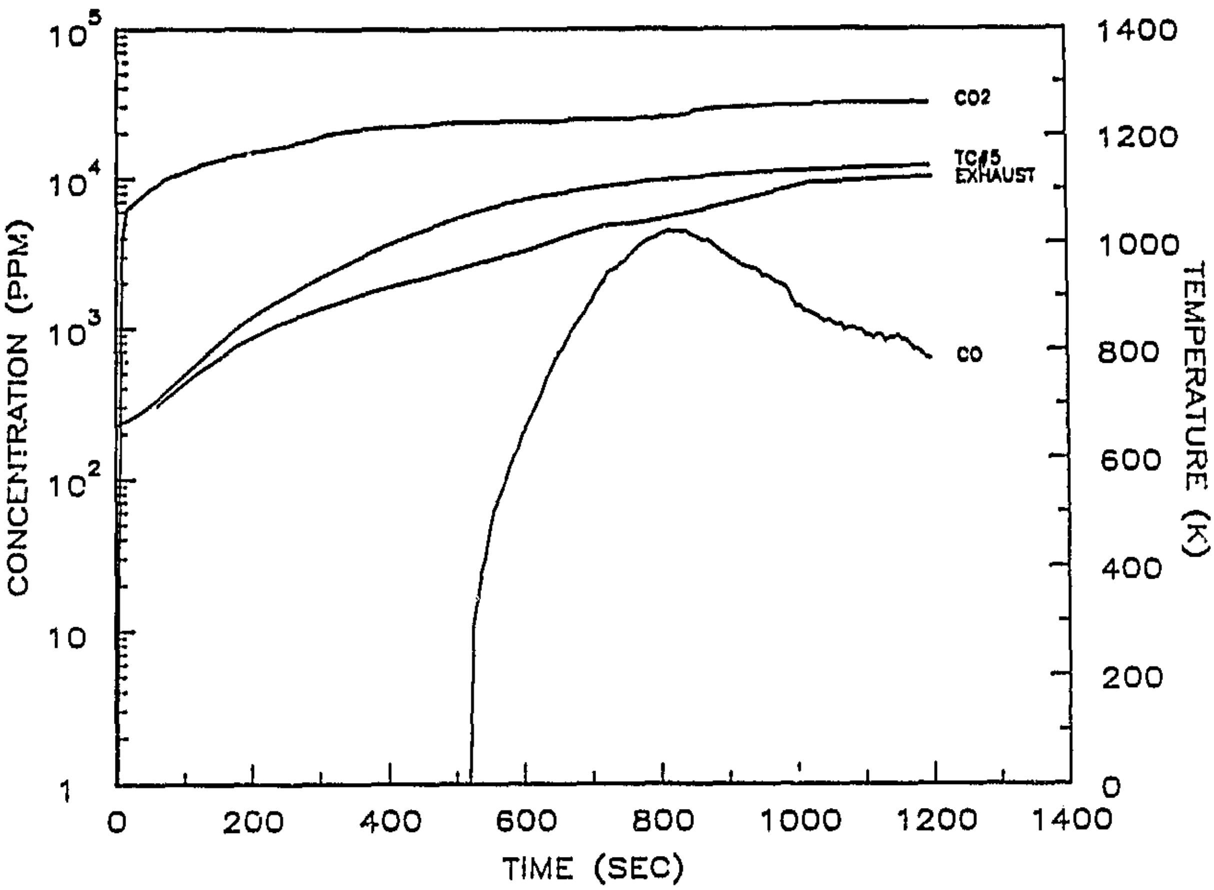

Figure 5. Transient exhaust gas carbon monoxide and carbon dioxide concentrations and temperature: Inlet temperature = 700°K, propane/air equivalence ratio = 0.3, reference velocity = 6 m/s.

immediately after the fuel is turned on, due to the oxidation of the propane on the catalyst surface, to a value of 6000 PPM which corresponds to a propane conversion efficiency of 5%. After this sudden increase in $CO_2$ the catalyst surface is totally covered and the conversion becomes controlled by the surface reaction rate. As the surface temperature increases (TC #5) the surface reaction rate increases resulting in a slow increase in the $CO_2$ emissions. It is not clear from these results when and to what extent the catalyst's performance becomes diffusion controlled before it reaches steady state.

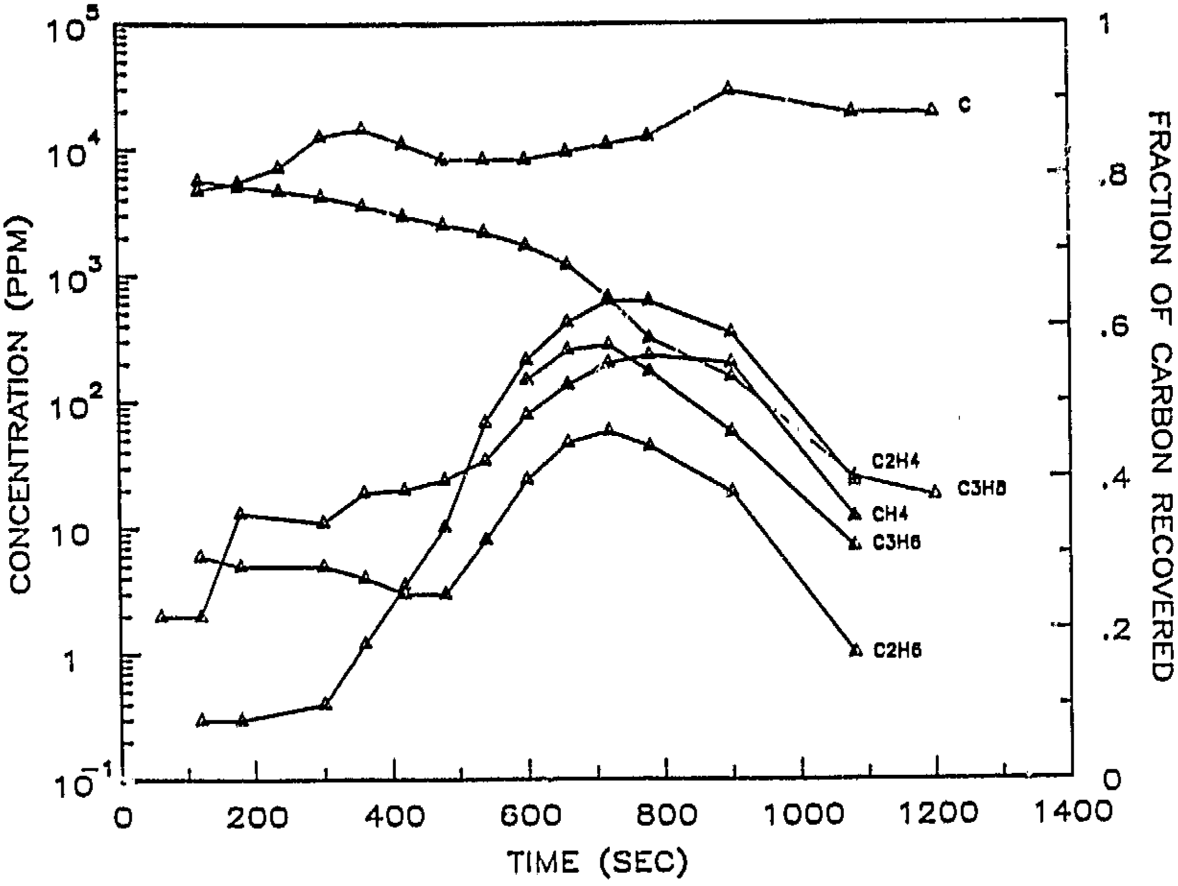

Figure 6. Transient exhaust gas hydrocarbon concentrations: Inlet temperature = 700°K, propane/air equivalence ratio = 0.3, reference velocity = 6 m/s.

At approximately 550 seconds after the fuel is turned on, CO appears in the exhaust (Figure 5). The CO concentration increases to a maximum of 5000 PPM at 800 seconds and then decreases to a steady state level of less than 1000 PPM. The appearance and subsequent disappearance of CO are due to gas phase reactions, since under these conditions it is well established that propane oxidizes directly to water and carbon dioxide on platinum catalysts.

The transient hydrocarbon emissions (Figure 6) are consistent with the explanation for CO and $CO_2$ emissions. The propane concentration decreases without any significant intermediate hydrocarbon concentrations until approximately 500 seconds when the gas temperature becomes sufficiently high for the gas phase reactions to begin. Once the gas phase reactions begin, some of the propane breaks down into C1 to C3 hydrocarbons. As the gas temperature increases, but slightly before the CO peak in Figure 5, the intermediate hydrocarbon concentrations peak. As the gas temperature increases further the intermediate hydrocarbons are oxidized to form water and carbon monoxide. And as shown in Figure 5 the carbon monoxide is then oxidized to form carbon dioxide. This behavior of the carbon monoxide and intermediate hydrocarbons is very similar to what has been observed by others in purely gas phase reactions under nearly identical conditions. Similar even in terms of the relative concentrations of the intermediate hydrocarbons and the fact that the hydrocarbons peaks before the carbon monoxide. This similarlity suggests that there is not a strong or pronounced effect of the surface reactions on the gas phase reactions.

Figure 7 shows the effect of lowering the equivalence ratio to 0.25 on the transient hydrocarbon emissions. We see the onset of gas phase reactions as indicated by the rise in the intermediate hydrocarbon concentrations, however, the reactions do not go to completion and there are significant unburned hydrocarbon emissions at steady state. This result shows the important role of gas phase reactions in achieving high combustion efficiency in catalytic combustors.

The effect of reference velocity on CO and $CO_2$ emission is shown in Figure 8. As the gas velocity increases the $CO_2$ emissions are found to decrease which is primarily due to the shortened residence time. The 3 m/s and 6 m/s cases show evidence of the onset of gas phase reactions by the

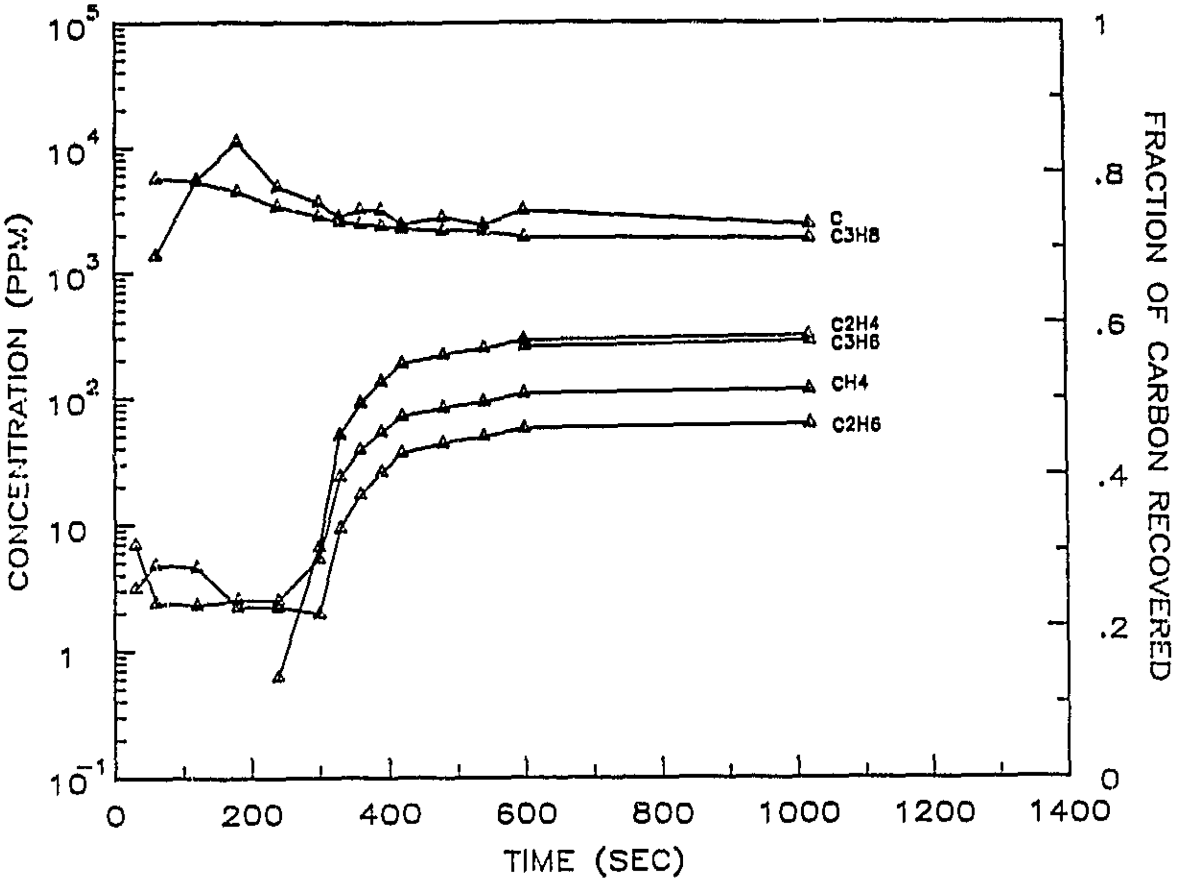

Figure 7. Transient exhaust gas hydrocarbon concentrations: Inlet temperature = 700°K, propane/air equivalence ratio = 0.25, reference velocity = 6 m/s.

increase in CO emissions at approximately 600 seconds and 300 seconds, respectively. As the gas velocity is increased from 3 m/s to 6 m/s, the convective heat transfer from the front of the catalyst bed increases causing the gas phase reactions to begin earlier. However, as the gas velocity is further increased to 12 m/s the effect of shortened residence time dominates and the onset of gas phase reactions is not observed. These CO results demonstrate the valuable insights that can be gained from the transient ignition measurements. Attempting to explain the steady state CO emissions results without the transient results would have been very difficult.

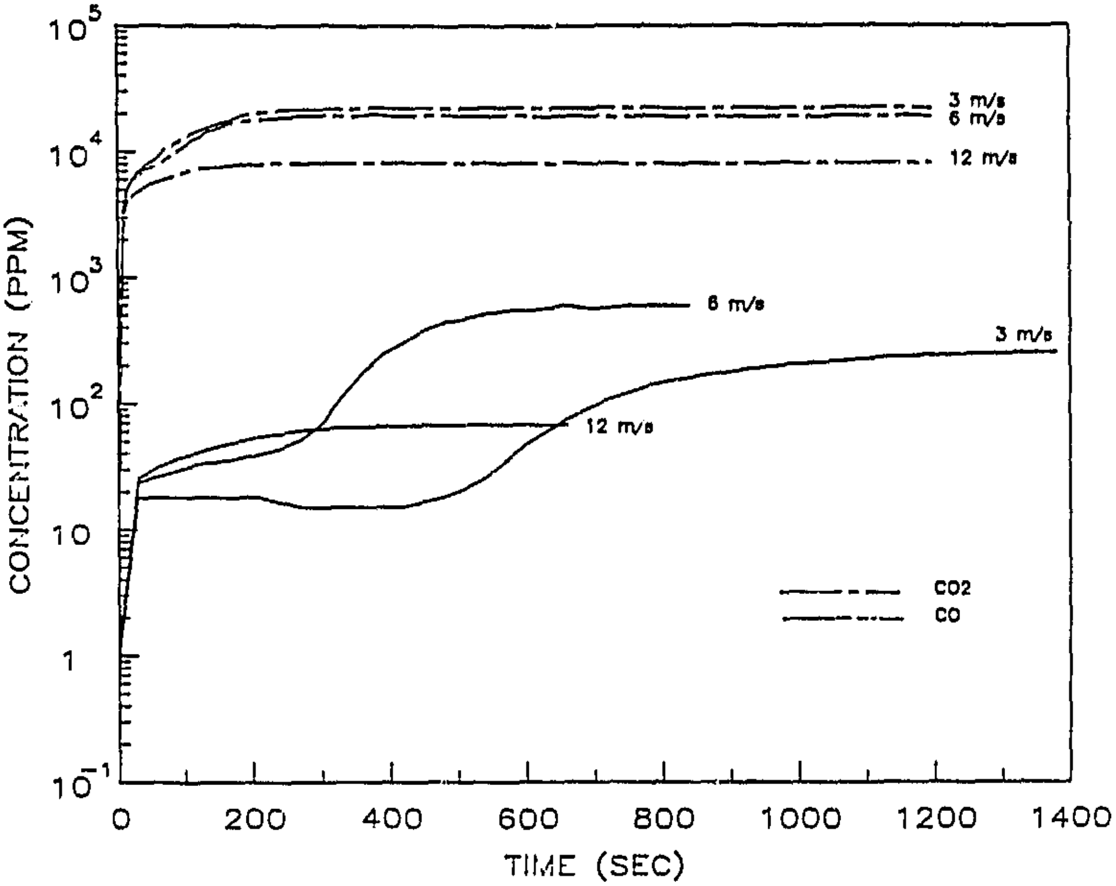

Figure 8. Transient exhaust gas carbon monoxide and carbon dioxide concentrations: Inlet temperature = 700°K, propane/air equivalence ratio = 0.25.

OH Measurement Results

Attempts were made to detect OH radicals within and at the exit of the catalyst bed at propane in air equivalence ratios of 0.25 and 0.3, reference velocities of 3, 6 and 12 m/s, and at inlet temperatures up to 700°K with no success. It was only by increasing the equivalence ratio to 0.35 at an inlet temperature of 700°K and reference velocity of 3 m/s that we were able to detect OH at the exit of the catalyst bed. The transient CO, $CO_2$ and hydrocarbon emissions for this case are shown in Figures 9 and 10.

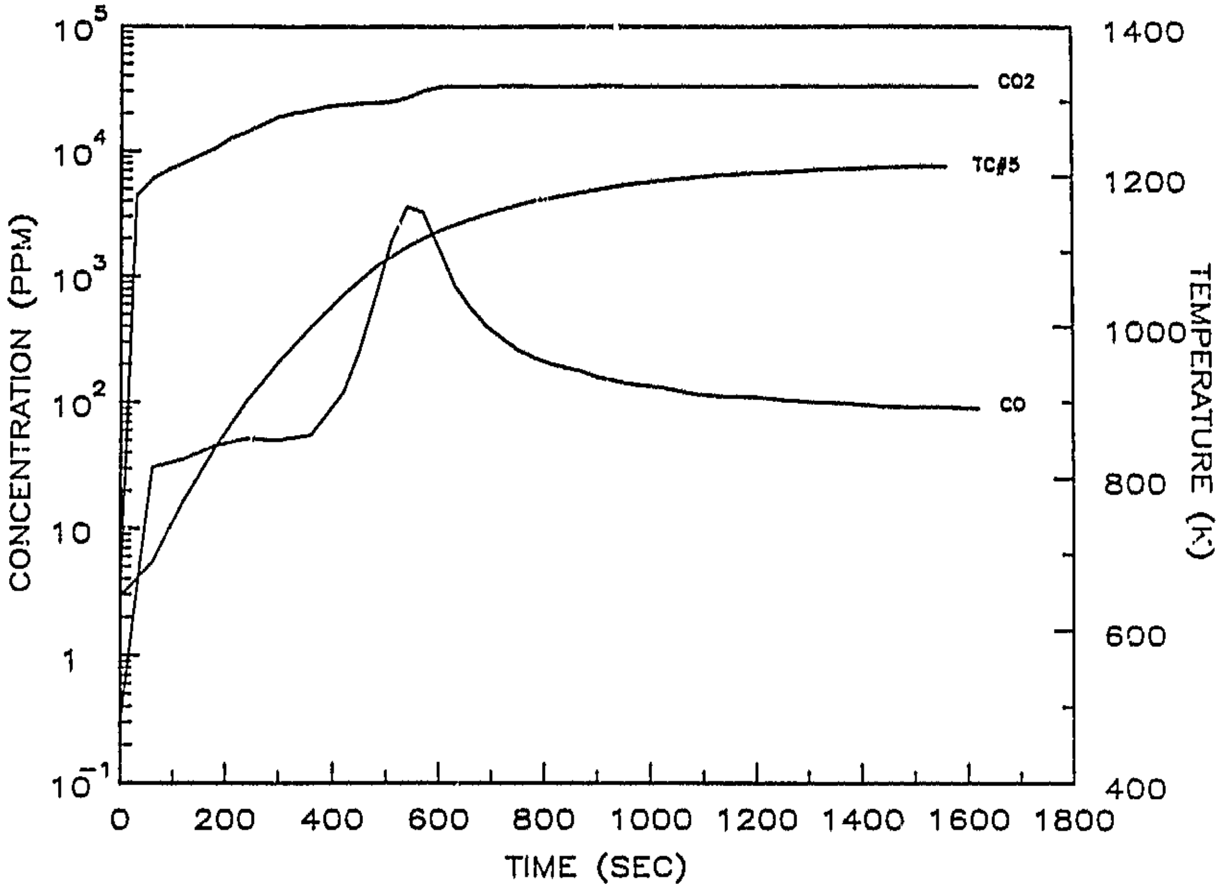

Figure 9. Transient exhaust gas carbon monoxide and carbon dioxide concentrations: Inlet temperature = 700°K, propane/air equivalence ratio = 0.35, reference velocity = 3 m/s.

As observed previously the occurrence of gas phase reactions is evident by the peak and subsequent consumption of the intermediate hydrocarbons and carbon monoxide. The corresponding transient OH concentration measurement is shown in Figure 11. As has been observed under gas phase conditions the OH concentration begins to increase in the post-flame region after the disappearance of the intermediate hydrocarbons and carbon monoxide, reaching a steady state level in the downstream post-flame gases which corresponds to

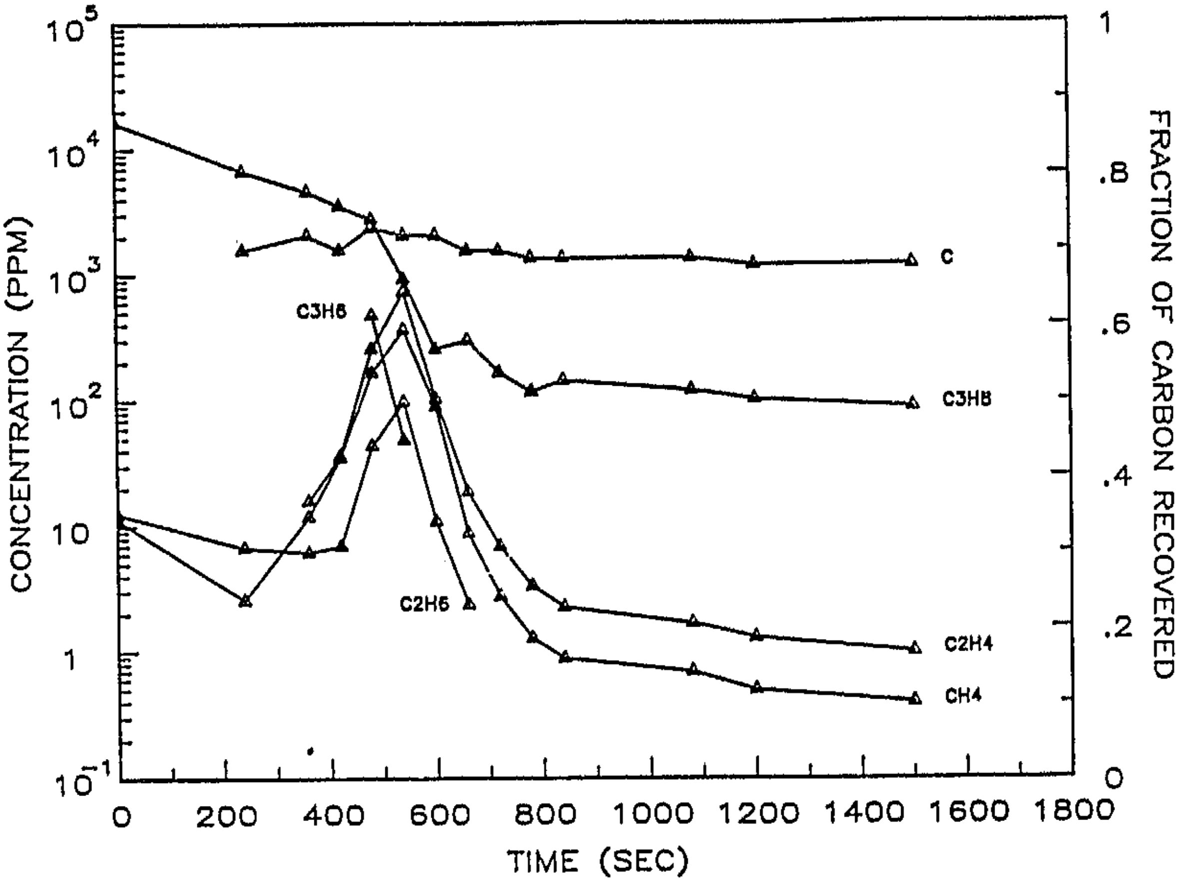

Figure 10. Transient exhaust gas hydrocarbon concentrations: Inlet temperature = 700°K, propane/air equivalence ratio = 0.35, reference velocity = 3 m/s.

its equilibrium value. The LIF measurement from which Figure 11 was obtained was calibrated by assuming that the steady state OH concentration was equal to the equilibrium OH concentration based on the overall equivalence ratio and the exhaust gas temperature. One notable discrepancy between this result and the purely gas phase reaction result is the absence of an OH radical overshoot. This suggests the possibility that the platinum catalyst is acting as a source of OH radicals, which is very reasonable given the presence of water and the high surface temperature, and that the steady state OH

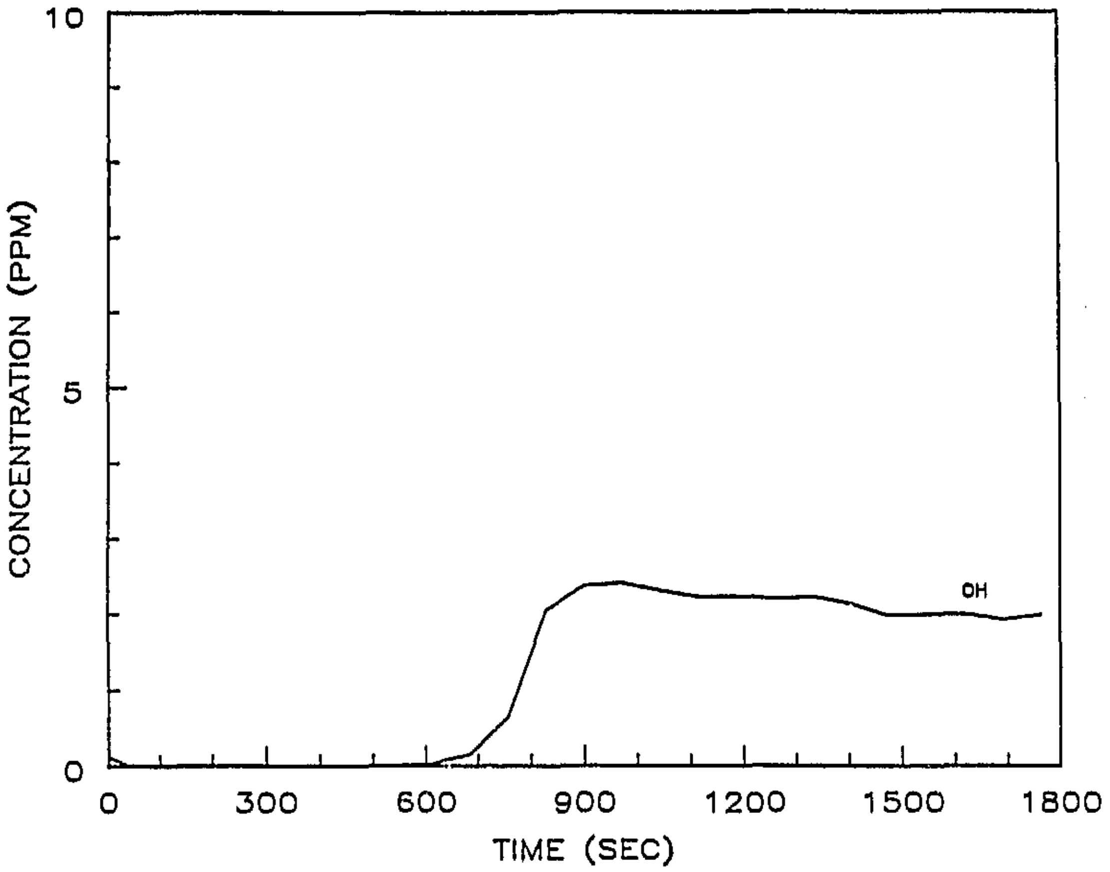

Figure 11. Transient exhaust gas hydroxyl radical concentration: Inlet temperature = 700°K, propane/air equivalence ratio = 0.35, reference velocity = 3 m/s.

concentration is actually in excess of the equilibrium concentration. Unfortunately independent calibration of the OH measurement requires an absorption measurement but this was not possible because of the low OH concentrations.

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15. Supplementary Notes

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16. Abstract

Experiments were conducted in order to better understand the role of catalytic surface reactions in determining the ignition characteristics of practical catalytic combustors. Measurements of hydrocarbon concentrations, carbon monoxide and carbon dioxide concentrations, hydroxyl radical concentrations, and gas temperature were made at the exit of a platinum coated, stacked plate, catalytic combustor during the ignition of lean propane-air mixtures. The substrate temperature profile was also measured during the ignition transient. In these experiments, ignition was initiated by suddenly turning on the fuel and the time to reach steady state was of the order of ten minutes. The gas phase reactions, which were clearly observable from these measurements, showed no pronounced effect due to the catalytic surface reactions, except possibly the absence of a hydroxyl radical overshoot. The transient ignition measurements were found to be valuable in understanding the steady state performance characteristics.

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