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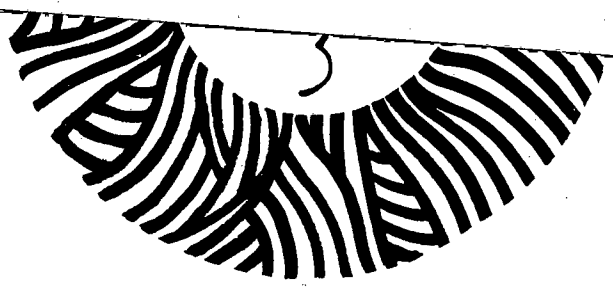
CATALYZED COMBUSTION OF LEAN FUEL/AIR MIXTURES

R. W. Schefer and F. Robben

April 1980

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CATALYZED COMBUSTION
OF LEAN FUEL/AIR MIXTURES

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ABSTRACT

A study has been made of the combustion characteristics of lean fuel/air mixtures flowing over heated catalytic and non-catalytic surfaces. The objective of the investigation was to develop a better understanding of the effect of a catalyst on the combustion process as the lean flammability limit of various fuels is approached. The fuels studied were H_2 , C_2H_6 , and C_3H_8 . Gas phase combustion ignition temperatures were determined over a range of equivalence ratios from boundary layer density profiles obtained using Rayleigh scattering. Surface reaction ignition temperatures and surface heat rates were also determined for the above fuels. A comparison of the results for a vacuum deposited platinum surface with results for a relatively "non-catalytic" quartz surface showed that the gas phase ignition temperature is a function of catalyst surface reactivity. At lower temperatures the quartz surface was essentially noncatalytic and resulted in gas phase ignition temperatures up to 100 K lower than with the platinum surface. At increased surface temperatures the catalytic activity of the quartz surface approached that of the platinum and gas phase ignition temperatures were identical for both surfaces. A detailed study of C_3H_8 oxidation on a platinum surface showed that for temperatures less than 670 K, CO is the primary oxidation product and for temperatures greater than 870 K, complete oxidation to CO_2 occurs.

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SECTION 1

INTRODUCTION

Lean combustion shows considerable promise as a means of reducing pollutant formation in combustion systems (1). However, the extent to which this concept can be effectively utilized is limited by the combustion characteristics of a particular fuel as its lean flammability limit is approached. Catalyzed combustion has been demonstrated to be effective in extending the stable burning region well below conventional lean gas phase flammability limits while at the same time providing low levels of unburned hydrocarbons and CO (2, 3). While preliminary tests have been quite promising, a number of aspects of catalyzed combustion are either not well understood or the necessary data are lacking. In the development of an optimum catalyst design for lean combustion applications it will be necessary to 1) develop a greater understanding of the role of the catalyst in the combustion process and 2) to determine high temperature catalytic surface reaction mechanisms and reaction rate data. It is the goal of this investigation to provide some of this necessary data for future catalytic combustion design development.

In the present study the surface ignition and gas phase ignition characteristics under conditions approaching the lean flammability limits of several fuel/air mixtures were investigated for boundary layer flow over a heated surface. The fuels used in the study were H_2 , C_2H_6 , and C_3H_8 . To better determine the effect of the catalyst on the combustion process both a catalytic platinum surface and a relatively noncatalytic quartz surface were utilized in the study. Results are also presented on a detailed study of lean C_3H_8 oxidation over a platinum surface.

SECTION 2

EXPERIMENTAL PROCEDURE

Details of the experimental system used in the present investigation have been described in References 4 and 5. Briefly, the configuration consists of a quartz plate with vacuum deposited platinum heating strips mounted as one wall of a 5 cm square, open, atmospheric jet of premixed fuel and air. The gas flow is parallel to the plate surface and results in the formation of a velocity and thermal boundary layer in the region near the wall surface. Control of the surface temperature is provided by five platinum heating strips which have been vacuum deposited on the quartz plate and can be electrically heated to temperatures approaching 1400 K. The heating strips are oriented perpendicular to the flow and are of varying widths to improve temperature control near the plate leading edge. The extent to which gas phase combustion and surface reaction occurs can thus be controlled through variations in plate surface temperature and fuel/air mixture ratio.

Surface temperatures greater than 1000 K were measured using a disappearing filament type optical pyrometer and an emissivity of 0.65 for the platinum surface. Surface temperatures below 1000 K were determined from the measured resistivity of the platinum strips and, independently, with a laboratory built infrared detector. Using this technique plate surface temperatures could be measured to an estimated accuracy of ± 15 K.

In the present investigation the platinum catalytic surface was provided by orienting the quartz plate so that the side with the platinum heating strips was directed toward the flow. To obtain a "noncatalytic" surface the plate was reversed so that the uncoated quartz surface was directed toward the flow.

The presence of gas phase combustion in the boundary layer was determined from total gas density profiles measured using Rayleigh scattering. As discussed in Reference (5), the boundary layer density profiles are self similar along the plate when no gas phase combustion is present. However, heat release due to gas phase combustion results in density profiles characterized by a more positive curvature in the high temperature region near the plate surface and an increase in thermal boundary layer thickness. To determine the gas phase ignition temperature the equivalence ratio was fixed at a desired value and the plate surface temperature was increased in steps of 25 K. After each increase in surface temperature the system was allowed to come to steady state and the boundary layer was traversed using Rayleigh scattering to measure the resulting gas density profile. A comparison of these profiles with profiles for no fuel added at the same surface temperature then made it possible to determine that temperature, defined as the gas phase ignition temperature, at which heat release due to gas phase combustion resulted in a detectable departure from self-similar behavior. The results presented in this paper were based on an analysis of density profiles at a distance of 50 mm from the heated wall leading edge since at distances greater than this, fluctuations in the jet mixing layer become a significant source of disturbance to the boundary layer flow.

To determine steady state surface energy release rates the plate temperature was initially adjusted to the desired value with no fuel present in the flow. This was done by varying the power input to the individual heating strips. Typically strips 1 and 2 required greater power inputs for a constant plate temperature due to the higher heat transfer coefficient near the heated wall leading edge. Fuel was then added to the flow, which increased the surface temperatures to some higher nonuniform value due to surface energy release. The power inputs to the individual strips were then decreased until the desired temperature was again reached. The resulting difference in power input to each strip, with and without fuel addition, is equal to the average heat release due to surface chemical reaction for that particular strip provided heat losses due to other sources remain constant. For a given plate temperature radiative losses are constant. Experimental measurements and numerical calculations have also shown that the boundary layer temperature profiles are

self-similar when no gas phase combustion is present, thus losses due to convection and conduction will remain constant for a given free stream velocity at temperatures lower than the gas phase ignition temperatures.

In the present investigation the surface reaction ignition temperature was defined as the surface temperature at which, for a given equivalence ratio, measurable heat release due to surface reaction was present. All results presented in the following sections were taken at a constant free stream velocity of 1.5 m/s under laminar flow conditions.

SECTION 3

RESULTS AND DISCUSSION

Surface Ignition

The dependence of surface ignition temperature on stoichiometry is shown in Fig. 1 for C_3H_8 /air and C_2H_6 /air mixtures flowing over a platinum surface. In both cases the surface ignition temperature was found to be only a weak function of equivalence ratio over the range of conditions investigated. That is, a small decrease in ignition temperature was observed as the equivalence ratio was increased toward stoichiometric conditions. The minimum ignition temperatures measured for C_3H_8 were approximately 470 K and, for C_2H_6 , somewhat higher at 700 K. These results agree well with the data of Hiam, et al. (6), who investigated the catalytic oxidation of C_3H_8 and C_2H_6 on a platinum filament. It should be noted that the corresponding ignition temperatures for gas phase reaction are significantly higher than those shown in Fig. 1 and therefore the observed increase in surface temperature is due to surface reaction only.

Gas Phase Ignition

Gas phase ignition temperatures for H_2 , C_3H_8 , and C_2H_6 on both platinum and quartz surfaces are shown in Figs. 2 through 4 as a function of equivalence ratio. In all cases at higher equivalence ratios a relatively weak dependence of ignition temperature on equivalence ratio was observed. However, as the equivalence ratio was reduced a much stronger dependence is noted. In the case of H_2 (Fig. 2) on a platinum surface minimum gas phase ignition temperatures of approximately 1000 K were observed at an equivalence ratio of 0.3. At lower equivalence ratios the ignition temperature rapidly

increased to a value of 1220 K at $\phi = 0.1$. This behavior was characteristic of all fuels investigated, that is a weak dependence of ignition temperature on equivalence ratio at higher equivalence ratios and a rapid increase in ignition temperature as the equivalence ratio was reduced.

With the quartz surface at lower surface temperatures, ignition occurs at approximately 100 K lower than with the platinum. The differences in ignition temperature decreases as the equivalence ratio is reduced until at an equivalence ratio of 0.1 identical ignition temperatures of 1220 K are achieved with both surfaces. Similar results were obtained with C_3H_8 and C_2H_6 . In both cases at an equivalence ratio of 0.9 ignition with the platinum surface occurred at approximately 1170 K and with the quartz surface it occurred at surface temperatures approximately 100 K lower. At an equivalence ratio of 0.5, where the ignition temperature was 1220 K for both fuels with a platinum surface, a difference in ignition temperature of only 25 K was observed in comparing the quartz and platinum surfaces.

This behavior is consistent with an increase in catalytic activity of the quartz surface at higher temperatures. Numerical calculations for H_2 /air mixtures flowing over a catalytic surface (7) have shown that catalytic reactions at the plate surface, particularly surface oxidation of the fuel and radical recombination, result in a suppression of gas phase reactions in the boundary. Thus, the increase in gas phase ignition temperature with respect to the platinum surface at higher surface temperatures would seem to imply an increase in catalytic activity which, at a temperature of 1220 K, equals that of the platinum in the case of H_2 . To verify this, surface heat release rates were measured for H_2 /air at an equivalence ratio of 0.2 flowing over a quartz surface. Assuming a one step model for surface reaction in which H_2 and O_2 react to form H_2O as a product ($\Delta H_R = 2.38 \times 10^8$ J/kg-mole) values for the surface reaction were calculated. Those results are shown as a function of surface temperature in Fig. 5. Note that the surface reaction rate for quartz has been normalized by the reaction rate for H_2 /air mixtures on a platinum surface obtained previously (8). At temperatures less than 870 K no surface reactivity was measured for the quartz surface. However, as the surface temperature was increased above 870 K, a gradual increase in surface reactivity relative to platinum was observed, followed by a rapid

increase at temperatures greater than 1170 K. At a surface temperature of 1220 K the catalytic activity of the quartz surface was equal to that of the platinum. Thus, it appears that the observed behavior in gas phase ignition characteristics for the platinum and quartz surfaces is due to the increased activity of the quartz surface at higher temperatures.

Propane Surface Oxidation Studies

Typical experimentally measured surface energy release rates for C_3H_8 /air are shown in Figs. 6 and 7 for plate temperatures of 670 K and 870 K and an equivalence ratio of 0.2. The free stream velocity was 1.5 m/s. As mentioned previously, the data points represent average values of the energy release rate over the individual heating strips and not local values. It can be seen that the maximum heat release rates occur at the plate leading edge and then rapidly decrease as one moves downstream. As discussed by Rosner (9), this behavior indicates that mass transfer effects are important under the above conditions. For viscous flow over a flat plate with reactions occurring at the surface, the transport of reactant species from the free stream to the plate surface varies with streamwise distance from the plate leading edge. Near the leading edge where the boundary layer is thin, convective and diffusive transport rates to the surface are rapid and the surface reaction rate approaches its kinetically limited value. Farther downstream the boundary layer becomes considerably thicker and transport rates to the surface are insufficient to prevent local reactant depletion near the surface. Under these conditions the surface reaction rate is limited by the maximum rate at which reactants can be transported to the surface.

Also shown are predicted local surface heat release rates calculated using a computational scheme developed previously (7). Briefly, the program uses a finite difference approach to solve the two dimensional boundary layer equations for flow over a flat plate surface with simultaneous gas phase and surface reactions. In the present application, no gas phase reactions are assumed to occur and the program is used to describe the convective/diffusive transport of reactant and product species through the boundary layer to and from the plate surface. Surface reactions are included in the calculations in the form of a species boundary condition at the surface in which the rate

of diffusion of a particular specie to the surface is equal to the surface reaction rate. The rate expression used to describe C_3H_8 oxidation at the plate surface is based on the work of Hiam, et al. (6) and is given by

$$R_S = 1.1 \times 10^7 [H_2] \exp(-17000/RT) \frac{\text{kg moles}}{\text{m}^2 \text{s}} \quad (1)$$

where $[H_2]$ is the concentration of H_2 at the surface (kg moles/m^3). Initial modelling calculations were based on the assumption of a one step reaction in which C_3H_8 and O_2 react at the surface to form CO_2 as the product. These results are indicated by the solid lines in Figs. 6 and 7. As can be seen in Fig. 7, the predicted and experimental results agree well at temperatures greater than 870 K. However, at 670 K it was found that the predicted heat release ratios were approximately a factor of 2 higher than those measured experimentally. If it is assumed that only partial oxidation of C_3H_8 to CO occurs at the surface at lower temperatures then, as shown by the dashed line in Fig. 6, good agreement is obtained with experimental results. These results agree qualitatively with the measurements of Marteney and Kesten (7) in which it was found that the ratio of CO_2 to CO in the product species from a catalytic reactor (utilizing a Matthey Bishop manufactured catalyst material) increased with increasing exhaust temperature.

An Arrhenius plot of experimentally measured average surface energy release rates for C_3H_8 as a function of inverse surface temperature for heating strips 1 and 2 is shown in Fig. 8. Predicted average surface heat release rates for strips 1 and 2 assuming CO_2 (solid line) and CO (dashed line) as the product species are also shown. Once again the transition from CO_2 to CO as the product of surface oxidation is apparent as the surface temperature is decreased from 870 K to 670 K. The effect of diffusion limited behavior on apparent activation energy is also shown. The slope of each curve at a given temperature is equal to E_A/R , where E_A is the apparent activation energy for surface oxidation of C_3H_8 and R is the gas constant. At higher surface temperatures the apparent activation energy is significantly less than the true activation energy. As the surface temperature is reduced the apparent activation energy approaches the true activation energy as the surface reaction rate becomes kinetically limited.

SECTION 4

SUMMARY

The effect of catalytic surface activity on gas phase and surface reaction ignition temperatures was studied for H_2 -, C_3H_8 -, and C_2H_6 -air mixtures flowing over a platinum and a quartz surface. It was found that the gas phase ignition temperature is a function of catalyst surface reactivity. That is at lower temperatures the quartz surface was essentially non-catalytic and resulted in gas phase ignition temperatures up to 100 K lower than with the platinum surface. At increased surface temperatures the catalytic activity of the quartz surface approached that of the platinum and gas phase ignition temperatures were identical for both surfaces. A detailed study of C_3H_8 oxidation on a platinum surface showed that for temperatures less than 670 K, CO is the primary oxidation product and for temperatures greater than 870 K, complete oxidation to CO_2 occurs.

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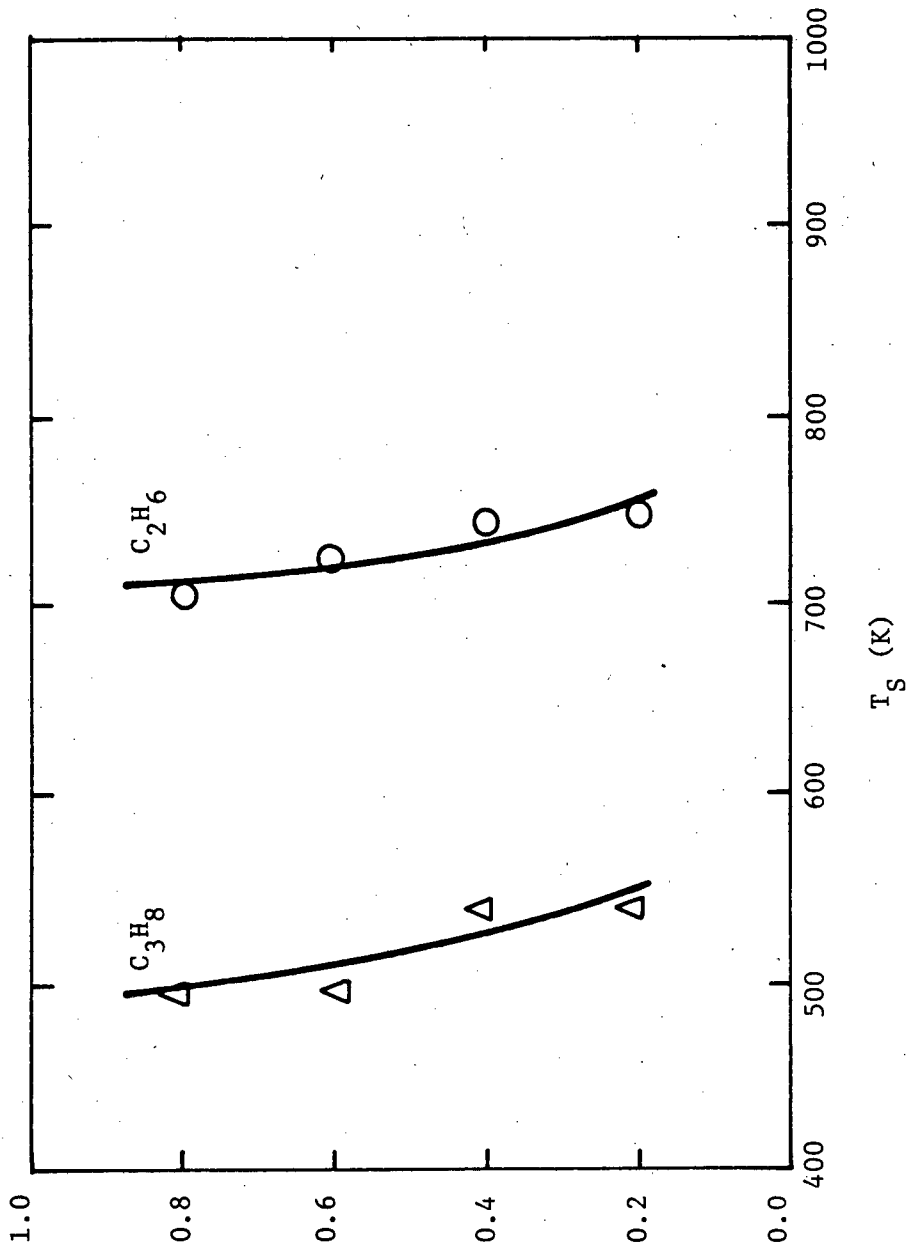


Fig. 1. Surface reaction ignition temperatures for C_3H_8 and C_2H_6 on a platinum surface. $U_\infty = 1.5$ m/s

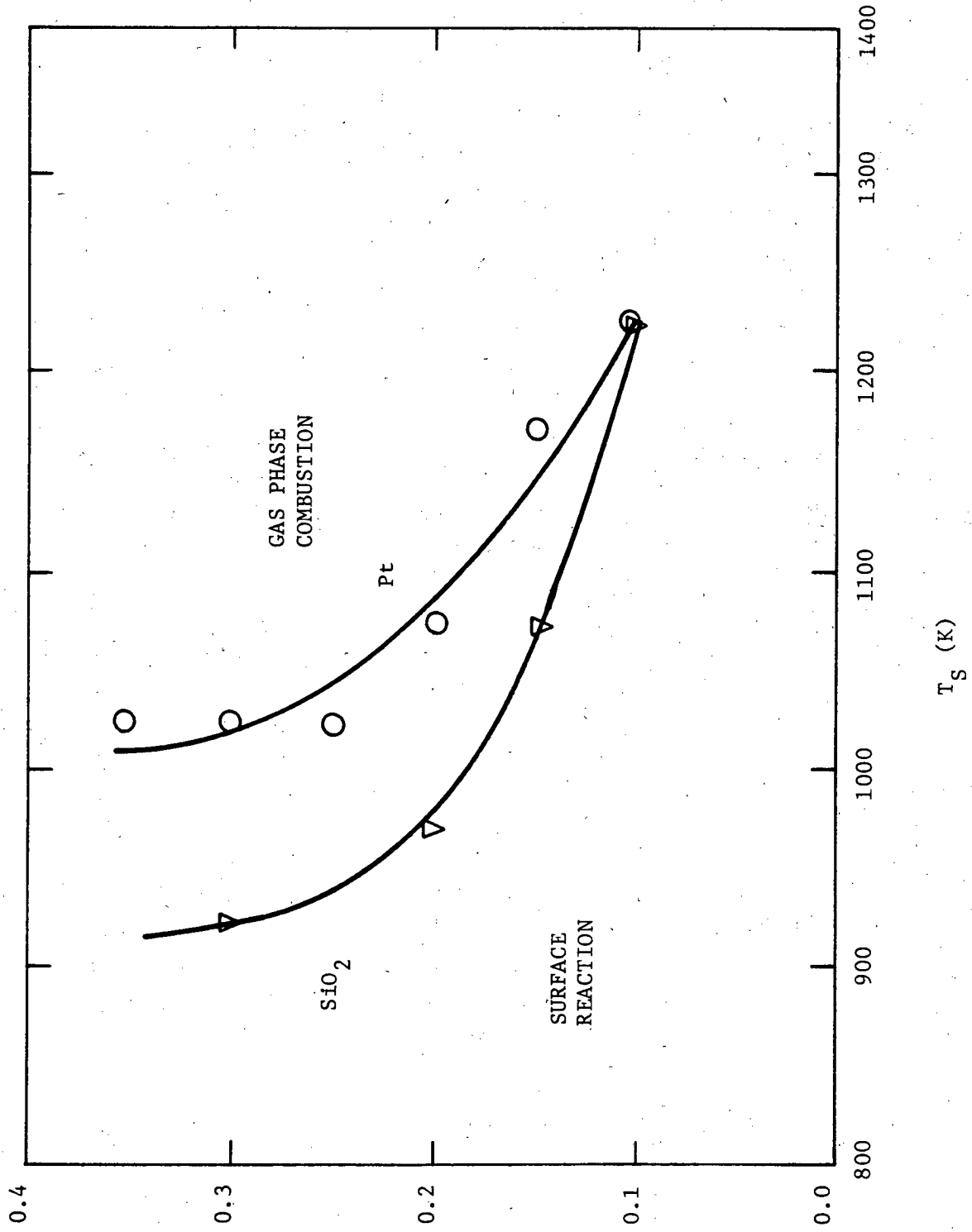


Fig. 2. Gas phase ignition temperatures for H₂/air combustion. $U_\infty = 1.5$ m/s

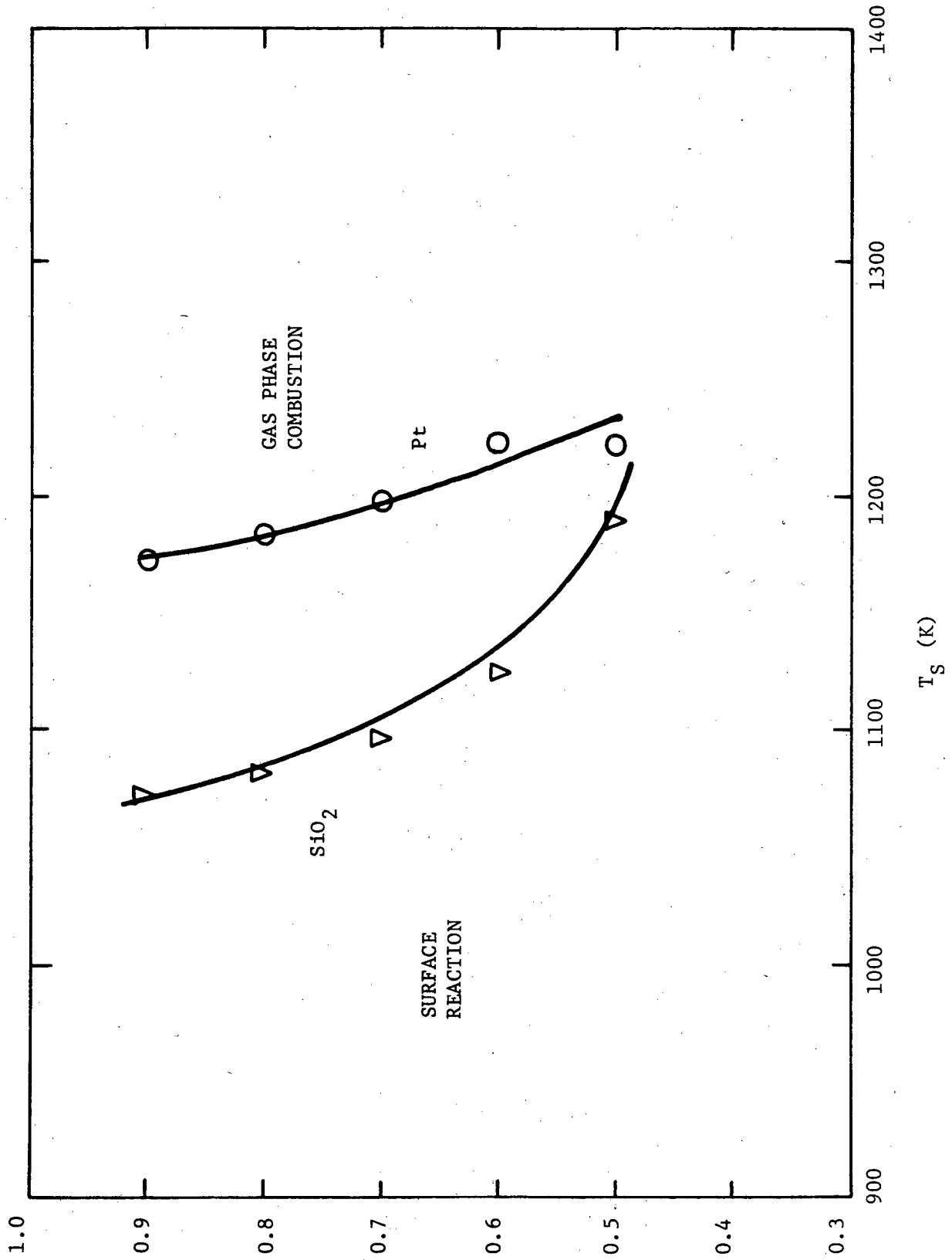


Fig. 3. Gas phase ignition temperatures for C_3H_8 combustion. $U_\infty = 1.5$ m/s

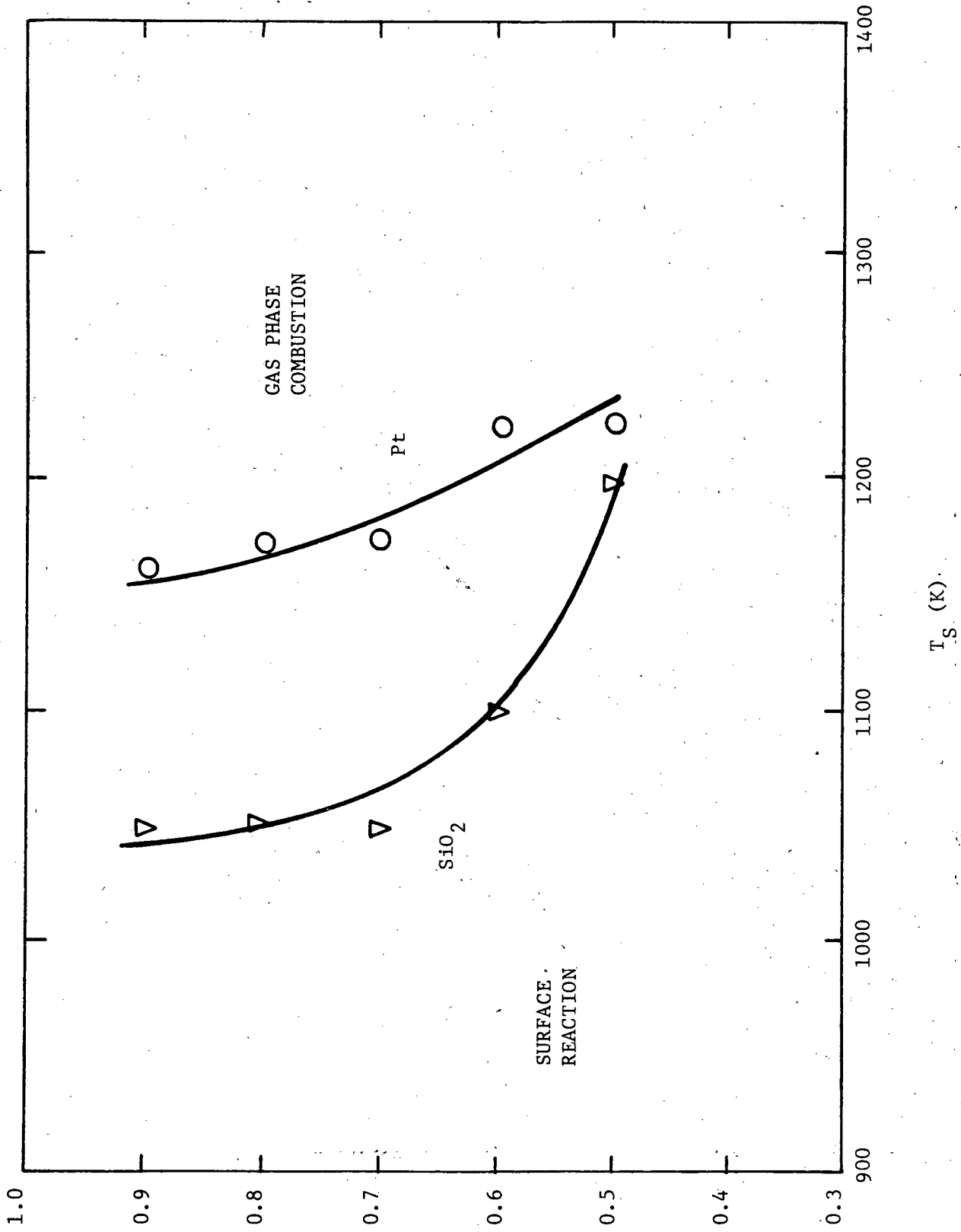


Fig. 4. Gas phase ignition temperatures for C_2H_6 combustion. $U_\infty = 1.5$ m/s

$$k_{\text{SiO}_2} / k_{\text{Pt}}$$

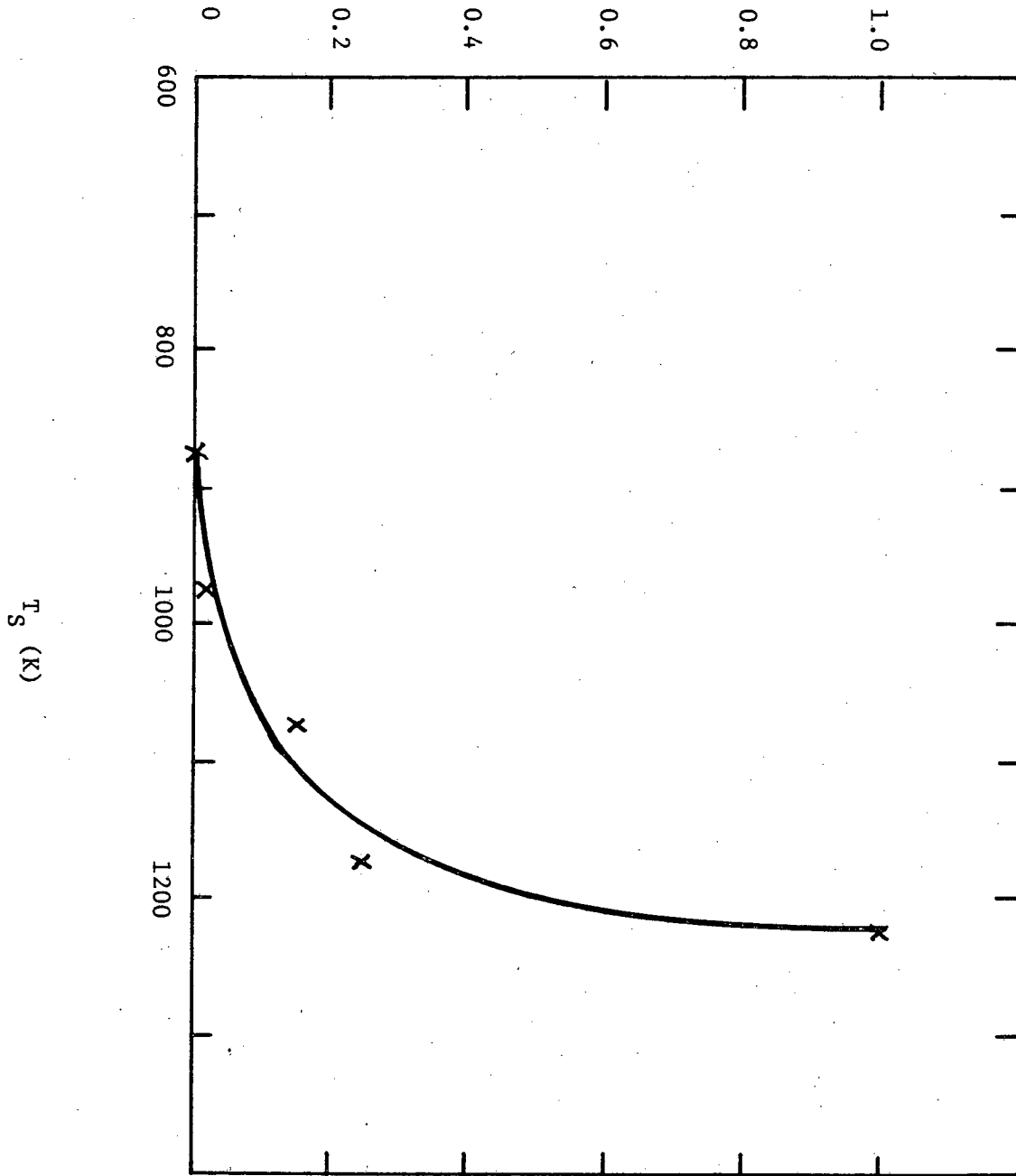


Fig. 5. Nondimensionalized surface reaction rate constant as a function of surface temperature for H_2 oxidation on a quartz surface.

$\phi = 0.2, U_\infty = 1.5 \text{ m/s}$

$$Q_s \text{ (J/m}^2\text{s)} \times 10^{-4}$$

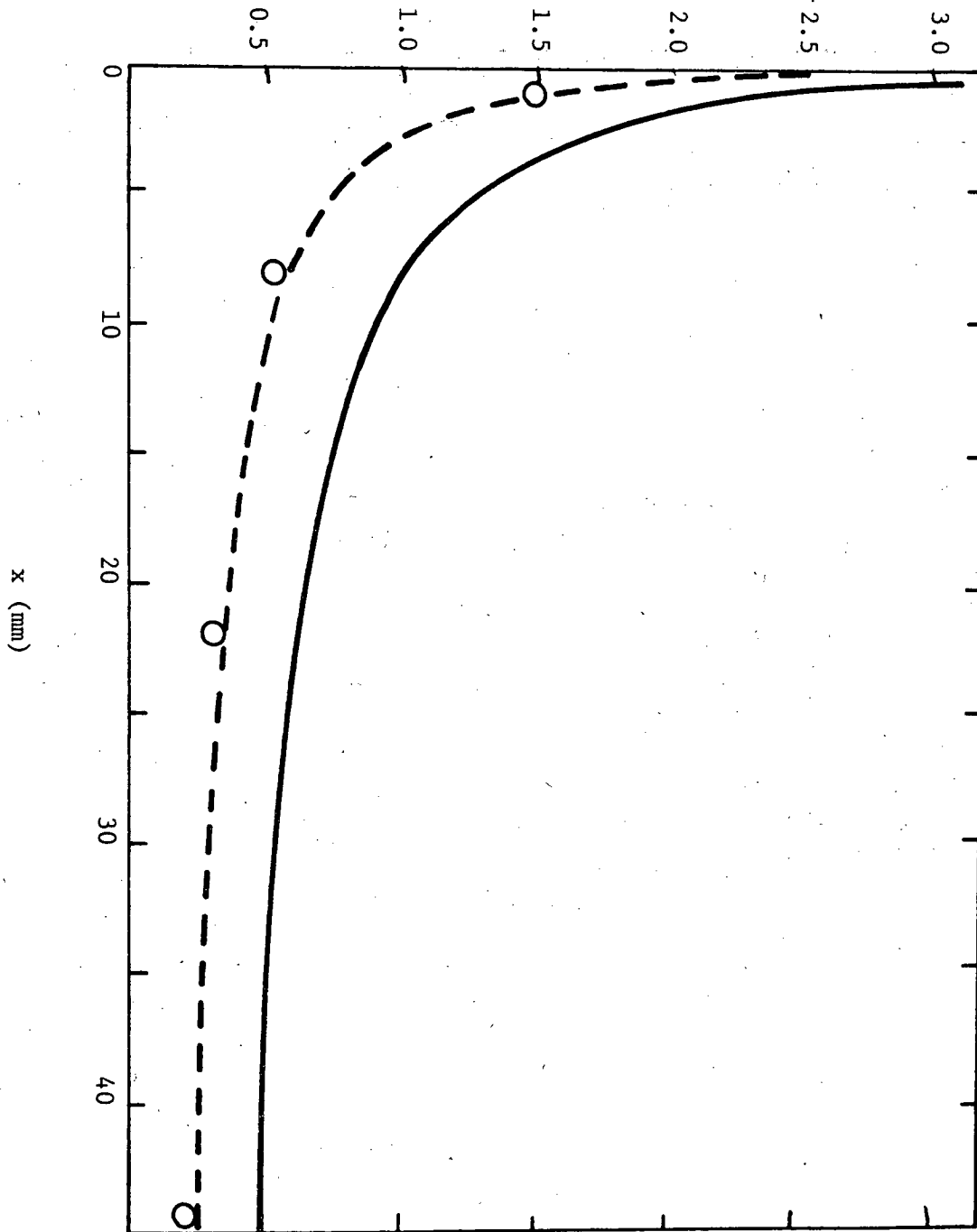


Fig. 6. Surface heat release rate as a function of distance along the plate for C_3H_8 /air combustion on a platinum coated plate. $T_s = 670$ K, $U_\infty = 1.5$ m/s, $\phi = 0.2$. Solid line indicates numerical results for oxidation to CO_2 ; dashed line indicates results for oxidation to CO.

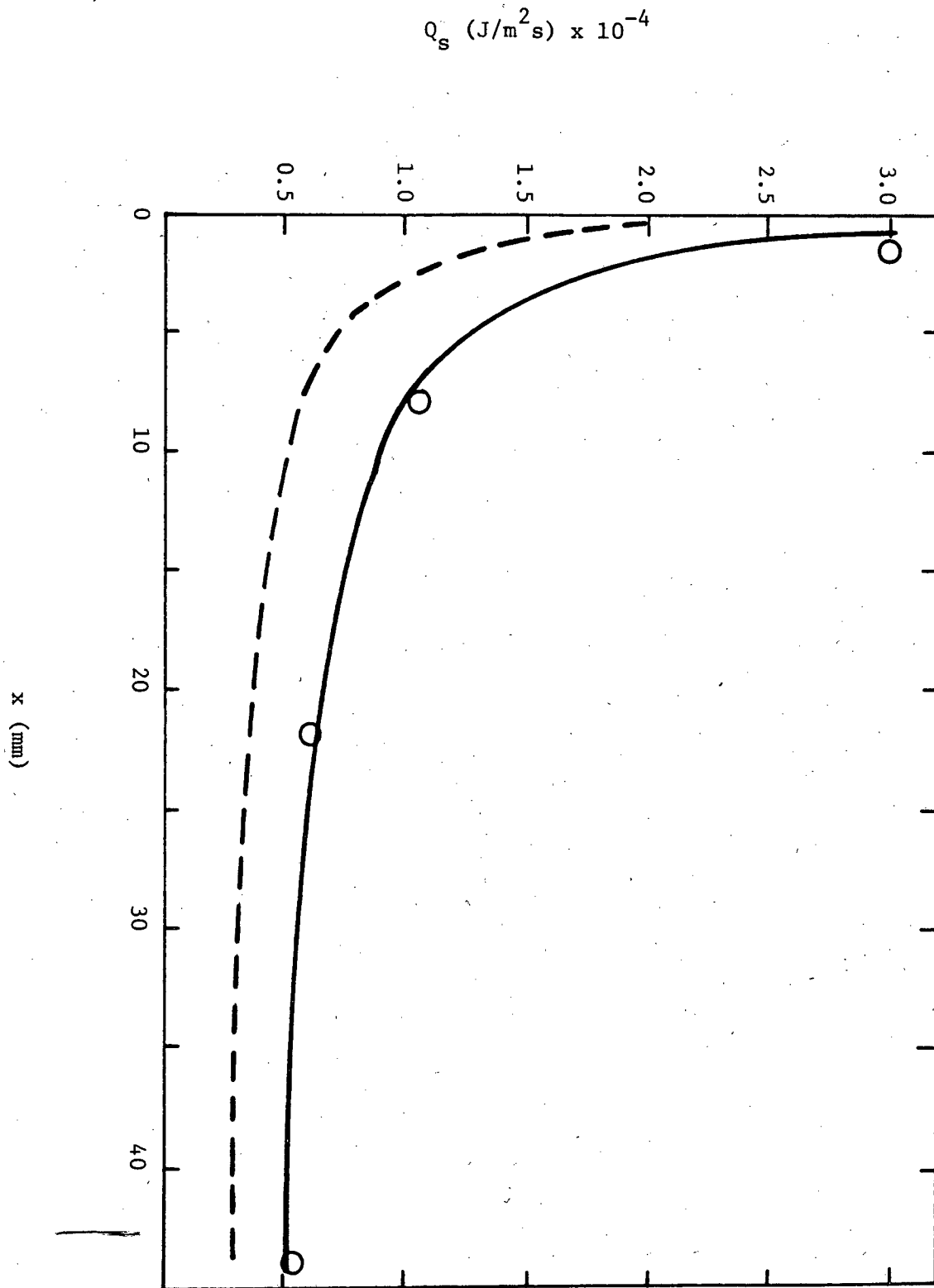


Fig. 7. Surface heat release rate as a function of distance along the plate for $\text{C}_3\text{H}_8/\text{air}$ combustion on a platinum coated plate. $T_s = 870$ K, $U_\infty = 1.5$ m/s, $\phi = 0.2$. Solid line indicates numerical results for oxidation to CO_2 ; dashed line indicates results for oxidation to CO .

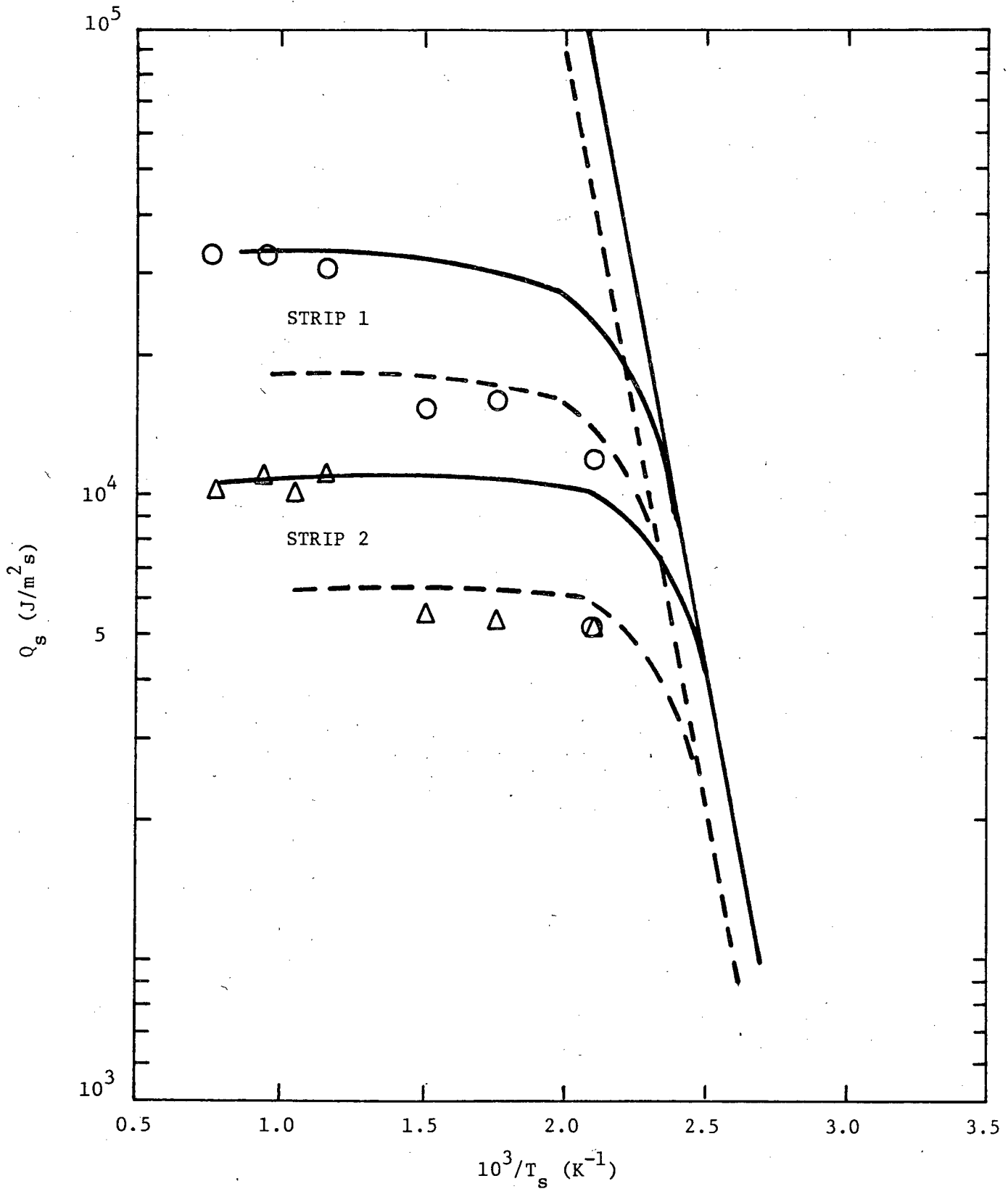


Fig. 8. Surface heat release rate as a function of inverse temperature for $\text{C}_3\text{H}_8/\text{air}$ combustion on a platinum coated plate. $\phi = 0.2$, $U_\infty = 1.5$ m/s. Solid line indicates numerical results for oxidation to CO_2 ; dashed line indicates results of oxidation to CO .

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