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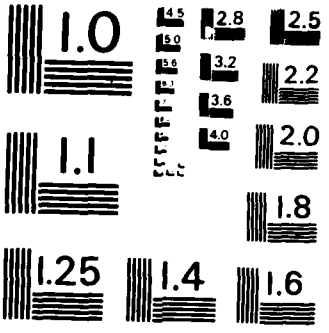

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A program of fundamental studies in catalytic combustion is described. Argon-diluted mixtures of fuel and oxygen were spontaneously reacted on platinum family surfaces. The specific surface reaction rate of fuel was obtained using an analytical program treating both mass transport and chemical reaction. Observed activation energies range from 5 Kcal/mole for propylene to 20 Kcal/mole for methane. Conditions of test varied from 250 to 500 C inlet at fuel-air equivalence ratios of 0.4 to 3.0.

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Two-fuel mixtures were studied to determine the extent to which a more-reactive component influences the system. For mixtures of 10% propylene in methane, the reaction is essentially the same as for propylene alone, although methane under similar conditions is nearly unreactive.

The condition of the surface was varied by pretreatment with fuel or oxygen. An extension in the transient time to steady operation was found, but neither suppression nor change in steady-state efficiency was seen, and the effect is entirely reversible.

Interaction of NO with hydrogen reactions was observed by addition of NO to inlet mixtures. A threshold temperature of 700 C appeared to be required for reduction in excess of 50%.

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INVESTIGATION OF THE KINETICS OF CATALYZED COMBUSTION

FINAL SUMMARY REPORT

P. J. MARTENEY

MAY 14, 1984

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STATEMENT OF PROBLEM

The work performed under this contract has been concerned with fundamentals of catalytic combustion. Interest in catalytic combustion stems from a continuing need for efficient, low-emissions combustion of gaseous and liquid fuels. In practice, most fuels are complex mixtures, and determination of the individual reaction rates would be difficult. As a first step, the reaction of a typical hydrocarbon, propane, was studied, and the reaction rate was determined with the assumption that propane is oxidized stepwise to carbon monoxide, then to carbon dioxide. The reaction rate of carbon monoxide on the surface was separately determined, using gas-phase reaction rates taken from the literature. The set of chemical and physical processes was continued in an analytical model developed previously at UTRC, and specific reaction rates were determined by matching the experimental temperature rise and extent of reaction.

In addition to the reaction rate of propane, the reaction of other simple hydrocarbon fuels was studied. The set of fuels included methane, ethane, ethylene, propane, and propylene, with additional studies of two-fuel mixtures, especially those containing methane or ethane with a very-reactive addend of ethylene or propylene. The latter scheme more appropriately represents mixtures having unlike fuels, as, for example, natural gas or light hydrocarbon mixtures.

A very useful feature of catalytic combustion is the apparent efficiency at both lean and rich conditions; the tests at UTRC have covered fuel/air equivalence ratios of 0.2 to 3.0. No evidence of soot formation has been found in these tests, although the equivalence ratio for gas-phase sooting is typically found to be approximately 1.8. (Only qualitative observations of soot were undertaken; soot formation or collection was not a specific part of this effort). A secondary question is the system start-up efficiency as a function of surface state under these off-stoichiometric conditions. As an attempt to determine what might occur in cycles of service and equivalence ratio, the catalytic surface was pretreated with either oxygen or fuel prior to admission of the normal mixtures, over a range of inlet temperatures and stoichiometries.

Finally, because of demonstrated value of catalytic combustion and afterburning or clean-up applications, the reaction of nitrogen oxides (NO_x) with fuel species was examined. Tests were conducted initially with nearly-equal quantities of fuel and NO, and subsequently (upon availability of higher-resolution analyzers) with small quantities of NO, some closely representing conditions which might pertain downstream of a slightly-inefficient burner producing thermal or fuel NO_x.

SUMMARY OF RESULTS

Principal among the efforts in these studies has been the determination of the reaction rate of hydrocarbons on the surface with variation in substrate material or geometry, active surface, and fuel. The determination of the reaction rate of propane was established as a central point of reference, since propane is readily catalyzed, but lies between other species in rate. As an adjunct to studies with propane, the rate of reaction of carbon monoxide was studied separately, since the model of propane reaction presumes conversion sequentially to carbon monoxide and carbon dioxide. The activation energy for propane reaction on platinum surfaces applied to square-cell cordierite substrate is estimated to be 9 Kcal/mole; for CO, the value is 15 Kcal/mole. Within these experiments, cell size was 25, 50, or 100 square cells per sq. in., with platinum loadings of 20 and 40 g/ft^3. The higher loading was found to exhibit only slightly higher activity, except in the case of 100 cells/in^2, in which a more-rapid onset of reaction occurred. However, this caused a short-term depletion of reactants on the surface, and overall a slightly-smaller extent of reaction. Through observations such as these, and use of the analytical model developed by UTRC, it is possible to determine whether a given system has been optimized.

The reaction rates of other hydrocarbons; methane, ethane, ethylene and propylene were also studied. In the catalytic system, differences in fuel reactivity are much greater than is found, for example, in gaseous flames. Ethylene and propylene are extremely reactive, having activation energies of 5 Kcal/mole or less. Ethane is slightly less reactive than propane, with an activation energy of approximately 15 Kcal/mole. Methane, at an inlet temperature of 300 C (at which the other fuels readily begin reaction) is, under the conditions of test used here, unreactive, and the activation energy is at least 20 Kcal/mole. However, a mixture of two fuels such as methane and propylene (or ethane and ethylene) tends to mimic the more-reactive component, and a mixture of 10% propylene in methane reacts nearly to the same extent as propylene alone. This is an important finding which aids in assessing the probability of efficient use of fuel mixtures, such as might be found in low BTU or process gases.

These investigations have not been restricted to the range of stoichiometries found in typical gas-phase combustion, because the catalytic limits are much wider. For example, propane fuel will initiate reaction at a temperature of 250 C on platinum surfaces over a range of equivalence ratios from 0.4 to 3.0. Blends with propylene or ethylene will react even more readily. (The limits of equivalence in these studies were 0.2 and 3.0; in most cases, conversion in the 1 inch-long reactor was too small for study at the lowest equivalence ratios, except at inlet temperatures near 500 C. However, the appearance of CO in products at these conditions qualitatively justifies the reaction model; viz, reaction of fuel to CO on the surface.

The condition of the active catalytic surface is known to play a part in the initiation of progress of reaction. In application, a catalytic system might be subject to a range of stoichiometries to determine the effect of this variation, the catalytic surface was pretreated with either

fuel or oxygen alone prior to testing. If species residing on the surface were sufficiently fixed, this could, in principle, prevent or seriously alter reaction. In these tests, the usual mixtures (minus an oxygen and fuel component) were passed through the catalyst for periods of up to 30 minutes, after which the missing component was added. There is a detectable lengthening of the time required for reaction to come to steady state, but not in the extent of reaction under steady operation. The indication is that the surface would not be poisoned by a shift in inlet composition, and that the temporary change is entirely reversible.

The interaction of fuel and nitrogen oxide (NO) on the surface was also studied. The NO was added to the inlet gas mixture, and outlet NO was measured. For addition of NO to propane mixtures, substantial reduction of NO is found for fuel/air ratios of 1.0 to 1.8 (studies at higher equivalence ratios were not pursued, because NO formation is strongly suppressed in all systems under very-rich conditions). Although there is a threshold reaction temperature of approximately 700 C, below which the reduction is much smaller, and sub-stoichiometric mixtures do not produce outlet temperatures this high, there is a slight reduction for lean mixtures. For rich mixtures, the reduction is as much as 50 to 70%.

PROPOSED TITLES OF JOURNAL ARTICLES

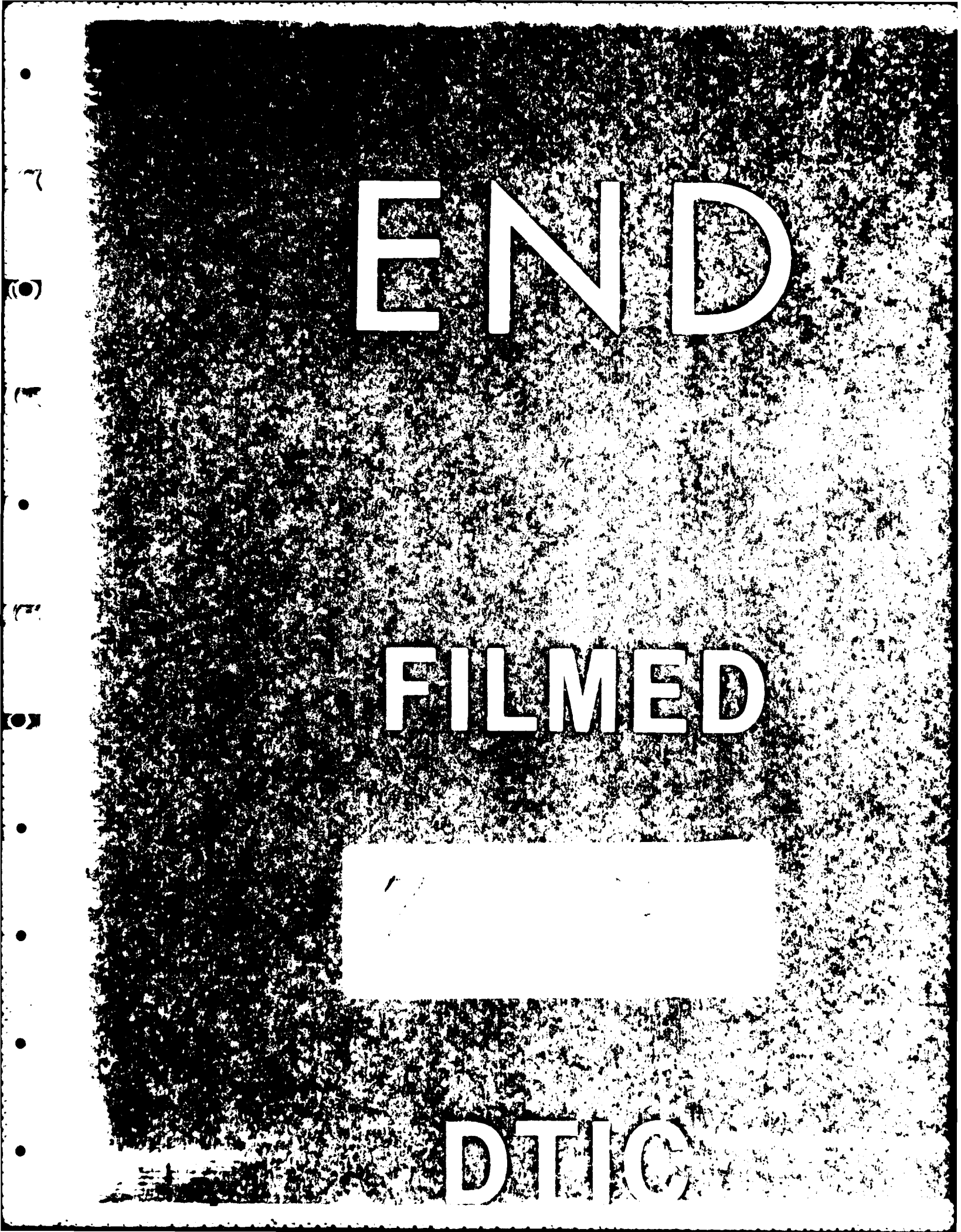
Author: P. J. Marteney

1. Catalytic Reaction of Carbon Monoxide and Propane on Platinum-Family Surfaces (Abstract Enclosed)

2. Reaction Rates of C_1 to C_3 Hydrocarbons in Catalytic Combustion

3. Catalytic Reaction of Mixed Hydrocarbon Fuels

4. Interaction of Hydrocarbon Fuels and Nitrogen Oxide (NO) during Catalytic Combustion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