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FORMATION AND CONTROL OF FUEL-NITROGEN POLLUTANTS
IN CATALYTIC COMBUSTION OF COAL-DERIVED GASES

Final Report

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MASTER

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CONTENTS	Page
Abstract	1
List of Tables	2
List of Figures	3
Acknowledgments	6
1. Introduction	7
2. Two-Dimensional Model	11
3. Experimental Apparatus	26
4. Experimental and Theoretical Results on Catalytic Oxidation of Carbon Monoxide	29
a. Experimental Results	29
b. Comparison of Computed and Measured Carbon Monoxide Data	32
5. Experimental Results on Medium-Btu Gas/Air	36
a. Medium-Btu Gas Having Negligible Sulfur and Nitrogen-Containing Impurities	36
b. Effects of Hydrogen Sulfide	40
c. Oxidation of Ammonia to Nitric Oxide	44
6. Optical Measurement of Gas Temperature and Species Concentrations	51
a. Proposed Systems for Making Measurements in a Catalytic Reactor	51
b. Pulsed, Multipass Technique for Enhancement of Raman Scattering	52
7. Conclusions	60
References	62
Figures	66
Appendix A: Radial Profiles of Gas Properties Upstream of the Catalytic Reactor	114
Appendix B: Experimental Results on Propane/Air	130

Abstract

The objective of this program has been the elucidation of the mechanism of high temperature catalytic oxidation of coal-derived gases, including their individual constituents, and the effects of sulfur and nitrogen impurities. Detailed experimental data were obtained and a two-dimensional model is being developed and tested by comparison with the experimental data. When complete, the model can be used to optimize designs of catalytic combustors.

The model at present includes axial and radial diffusion and gas and surface chemical reactions. Measured substrate temperatures are input in lieu of complete coupling of gas and solid energy conservation equations and radiative heat transfer. Axial and radial gas temperature and composition profiles inside a catalyst channel were computed and compared with experimental measurements at the catalyst outlet.

Experimental investigations were made of carbon monoxide and medium-Btu gas combustion in the presence of platinum supported on a monolithic Cordierite substrate. Axial profiles of substrate temperature, gas temperature, and gas composition were determined at different gas velocities and equivalence ratios. The effects of H_2S and NH_3 in the medium-Btu gas were also investigated.

Systems were proposed for making resonance absorption and Raman scattering measurements of gas temperature and/or species concentrations in a catalytic reactor. A new pulsed multipass Raman scattering technique for increasing photon yield from a scattering volume was developed.

LIST OF TABLES

Page

- 2-1. Nondimensional Governing Equations for Reacting Flow in a Circular Tube with Catalytic Wall.
- 3-1. Catalyst Properties
- 4-1. CO/Air Combustion in Pt/ γ -Al₂O₃/Cordierite Catalyst
- 5-1. Reference Conditions, Catalyst Pressure Drop, and Adiabatic Temperature for the medium-Btu Gas Runs.
- 5-2. Reference, Catalyst, and Outlet Conditions for Runs Using Hydrogen Sulfide Doped Medium-Btu Gas.
- 5-3. Species Mole Fractions and Equivalence Ratios for Runs Using Ammonia Doped Medium-Btu Gas.

LIST OF FIGURES

- 3-1. Flow reactor for the study of catalytic combustion.
- 3-2. Arrangement of the fuel injection grid.
- 3-3. Substrate temperature vs radial position, C_3H_8 combustion.
- 3-4. Arrangement of catalyst, flashback arrestor, and probes.
- 3-5. Oxidizer, fuel, fuel dopant, and sample flows.
- 4-1. Substrate and exhaust temperatures vs. axial position at different equivalence ratios, CO combustion.
- 4-2. Exhaust composition vs. axial position at different equivalence ratios, CO combustion.
- 4-3. Substrate and exhaust temperatures vs. axial position, CO combustion.
- 4-4. Substrate and exhaust temperatures vs. axial position, CO combustion.
- 4-5. Substrate and exhaust temperatures vs. axial position, CO combustion.
- 4-6. Exhaust composition vs. axial position at different reference velocities, CO combustion.
- 4-7. Observed and predicted ratios of unburned CO to inlet CO vs. reference velocity, CO combustion.
- 4-8. Observed and predicted pressure drops vs. reference velocity, CO combustion.
- 4-9. Arrhenius plot of rate coefficients for CO oxidation in the exhaust, CO combustion.
- 4-10. Calculated fuel mass fractions and gas temperatures vs. radial position, CO combustion.
- 4-11. Calculated fuel mass fractions and gas temperatures vs. axial position, CO combustion.
- 4-12. Calculated fuel mass fractions and gas temperatures vs. radial position, CO combustion.
- 4-13. Calculated fuel mass fractions and gas temperatures vs. axial position, CO combustion.

- 5-1. Substrate and gas temperatures vs. axial position at different reference velocities, medium-Btu gas combustion.
- 5-2. Unburned fuel species vs. axial position medium-Btu gas combustion.
- 5-3. Unburned fuel species at the catalyst exit vs. reference velocity medium-Btu gas combustion.
- 5-4. Unburned fuel species vs. axial position, medium-Btu gas combustion.
- 5-5. Unburned fuel species vs. axial position, medium-Btu gas combustion.
- 5-6. Unburned fuel species at the catalyst exit vs. adiabatic temperature, medium-Btu gas combustion.
- 5-7. Arrhenius plot of rate coefficients for CO oxidation in the exhaust; CO, medium-Btu gas, and C_3H_8 combustion.
- 5-8. Substrate temperature vs. mole fraction of H_2S in fuel, medium-Btu gas combustion.
- 5-9. Fraction of H_2 unconverted vs. mole fraction of H_2S in fuel, medium-Btu gas combustion.
- 5-10. Fraction of CO unconverted vs. mole fraction of H_2S in fuel, medium-Btu gas combustion.
- 5-11. Fraction of CH_4 unconverted vs. mole fraction of H_2S in fuel, medium-Btu gas combustion.
- 5-12. Maximum substrate temperature vs. adiabatic temperature, with and without H_2S , medium-Btu gas combustion.
- 5-13. Fraction of H_2 unconverted vs. adiabatic temperature, with and without H_2S , medium-Btu gas combustion.
- 5-14. Fraction of CO unconverted vs. adiabatic temperature, with and without H_2S , medium-Btu gas combustion.
- 5-15. Fraction of CH_4 unconverted vs. adiabatic temperature, with and without H_2S , medium-Btu gas combustion.
- 5-16. Fraction of NH_3 converted to NO vs. equivalence ratio, medium-Btu gas combustion.
- 5-17. Fraction of NH_3 converted to NO vs. equivalence ratio, medium-Btu gas combustion.
- 5-18. Fraction of NH_3 converted to NO, and mole fraction of NO vs. mole fraction of NH_3 at inlet, medium-Btu gas combustion.

- 6-1. Catalyst configuration and beam path for resonance absorption measurements.
- 6-2. Resonance absorption system for measuring species concentrations.
- 6-3. Catalyst configuration and incident and scattered beam paths for Raman scattering measurements.
- 6-4. Pulsed Raman scattering system for measuring species concentrations and gas temperature.
- 6-5. Normalized number of multipass photons vs. number of passes.
- 6-6. Enhancement of the effective signal to noise ratio after background subtraction.
- 6-7. Minimum detectable nitrogen concentration vs. number of passes with constant background noise.
- 6-8. Minimum detectable nitrogen concentration vs. number of passes with laser-induced background.
- 6-9. Pulsed multipass cell.
- 6-10. Pulsed multipass cell experiment.
- 6-11. Comparison of Rayleigh scattering signal for single pass and multipass cases.
- 6-12. Pulsed multipass Raman scattering experiment.

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1. Introduction

The technology and data base needed to incorporate catalytic reactors in practical heat and power systems are expanding rapidly. The work in progress includes development of catalytic combustors for aircraft gas turbines (Blazowski and Bresowar, 1974; Rosfjord, 1976; Siminski and Shaw, 1978; Szaniszlo, 1978; Angello and Rosfjord, 1979), stationary gas turbines (Pfefferle, et al., 1975; Carrubba, et al., 1976; DeCorso, et al., 1976; Krill and Kesselring, 1979; DeCorso and Carl, 1979), highway vehicle gas turbines (Anderson, 1977a, 1977b, 1978, 1979; Anderson, et al., 1977), and boilers (Krill and Kesselring, 1979). Other studies have focused on catalyst design for particular fuels such as low-Btu gases (Carrubba and Osgerby, 1978) and No. 6 oil (Pogson and Mansour, 1979). Still other work has been concerned with catalyst durability (Heck, et al., 1977). Demonstrated advantages of catalytic, when compared with conventional, combustion are:

- Lower emissions of HC, CO, NO_x, and smoke.
- Higher efficiency.
- Increased operational stability.
- Stable operation at lower equivalence ratios.
- Improved pattern factor.
- Wider fuel specification.

The objective of the present program has been the elucidation of the mechanism of high temperature catalytic oxidation of coal-derived gases, including their individual constituents, and the effect of possible impurities. The work has included collection of detailed experimental data, development of a two-dimensional model, and testing of its accuracy by comparison with the experimental data. When complete, the model can be used to optimize the design of catalytic combustors.

A number of physical and chemical processes have been suggested as important determinants of catalytic combustor performance (Lavid and Bracco, 1976; Kelly, et al., 1977; Pfefferle, 1978):

- axial and radial convection of species, heat, and momentum,
- axial and radial diffusion of species, heat, and momentum,
- axial heat transfer in substrate by conduction and radiation,
- gas and wall chemical reactions.

The authors are aware of only two theoretical studies which incorporate the following essential features:

- axial convection with variable gas velocity,
- radial heat and mass transport,
- variable wall temperature,
- gas and wall reactions.

Cerkanowicz, Cole, and Stevens (1977) modeled the steady state operation of a catalyst including one-step homogeneous and heterogeneous reactions, radial heat and mass transport, axial heat conduction in the solid, and axial variation in pressure and flow velocity. They assumed plug flow and constant transfer coefficients. The model predictions were compared with the experimental data of Pfefferle, et al., (1975) on catalytic combustion of propene. The model successfully predicted the transition from surface reaction to diffusion control, and the ignition of homogeneous reactions, as inlet temperature increases. It also correctly predicted the equivalence ratio at which homogeneous reaction is ignited with fixed inlet temperature. The model exhibited ignition-extinction hysteresis, which has also been observed experimentally.

Kelly, Kendall, Chu, and Kesselring (1977) modeled steady state operation using multiple homogeneous reactions, one-step wall reaction, axial heat and species diffusion, and axial substrate heat transfer by conduction and radiation. Flow velocity was variable, but pressure was fixed. Radial transport was treated using variable transfer coefficients. Studies with this model showed that a distinct light-off transition for homogeneous reactions depends on the inclusion of axial diffusion of both heat and species. The model predicted that blowout mass throughput and emissions both increase with increasing channel diameter. These observations led to the development of graded cell catalysts having improved performance (Kesselring, et al., 1977).

A major unresolved question concerns the effects of radial convection and diffusion on the rates of the homogeneous and wall reactions. These interactions are not properly accounted for in a one-dimensional description of the flow. One of the most needed improvements in the theory of combustion catalyst operation is therefore the removal of the assumption of uniform conditions across the channels. More extensive tests of model predictions by comparison with experimental data are also required to establish the models' reliability. A computer code which solves the two-dimensional equations describing combustion in catalytic channels is being developed in our laboratory. A parallel experimental program provides data for testing of the model.

Coal-derived low and medium-Btu gases may contain up to about 1 mole % NH_3 , depending on the gasification process, the nitrogen content of the coal, and the method of sulfur removal (Walsh, 1978). Several experimental investigations have been made on catalytic combustion of simulated low and medium-Btu Gases without bound nitrogen (Pfefferle, et al., 1975; Carrubba, et al., 1976; Carrubba and Osgerby, 1978). Without exception these studies showed that the amount of thermal NO_x produced in catalytic combustion of these fuels is extremely small (< 1 mol ppm). Thermal NO_x formation is avoided because peak gas temperatures are relatively low, and because residence times are sufficiently short.

Martin (1976) made a theoretical study of thermal and fuel NO_x formation in single and two-stage catalytic burners under conditions characteristic of an advanced, high inlet temperature stationary gas turbine. He assumed plug flow in the catalyst sections and included only homogeneous reactions in the model. When burning clean low-Btu gas in the single stage configuration, Martin found that thermal NO increased linearly with residence time, and that its rate of production increased with increasing pressure. The model predicted formation of 87 mol ppm (corrected to stoichiometric) for a pressure of 10 atm, adiabatic temperature of 1813 K, and residence time of 100 ms. Another calculation was done for the same conditions assuming that the fuel contained 4000 mol ppm NH_3 . 86% of the NH_3 was converted to NO, resulting in 890 mol ppm NO (as calculated) in the exhaust.

The two-stage configuration considered by Martin consisted of a rich primary zone followed by secondary air addition. The total nitrogen species ($\text{NO} + \text{HCN} + \text{NH}_3$) at the exit of the primary stage increased as the residence time in this zone was decreased. The minimum nitrogen species was observed at a primary zone equivalence ratio of 1.33 for all residence times. Martin notes that his mechanism predicts that removal of CH_4 from the fuel eliminates HCN formation, a result which might be used to help minimize NO_x production in combustion of coal-derived gases, since their CH_4 content is to some extent adjustable by variation of gasifier conditions. Calculations were done for two extreme rates of addition and mixing of the secondary air; instantaneous and gradual (55 ms). Gradual air addition caused a large temperature excursion resulting in formation of a high concentration of thermal NO in addition to the nitrogen species already present from the primary stage. Instantaneous mixing allowed only the formation of a smaller amount of prompt NO in addition to conversion of the primary stage nitrogen species to NO. The system was optimized by choosing the primary zone equivalence ratio which gave the minimum amount of nitrogen species ($\phi = 1.33$), a long residence time (500 ms), and by assuming instantaneous mixing of the secondary air. Final NO for this configuration was 150 mol ppm (corrected to stoichiometric).

Folsom, Courtney, and Heap (1979) made experimental measurements of NH_3 conversion to NO, NO_x , and HCN during combustion of a low-Btu gas in a single stage catalytic reactor. They added 471 mol ppm NH_3 to the fuel to approximate the composition of a low-Btu gas after low temperature cleanup. The fraction of NH_3 converted to nitrogenous species ($\text{NO} + \text{NO}_2 + \text{NH}_3 + \text{HCN}$) was a minimum in the range of 60 to 100% theoretical air. HCN and NH_3 predominate under rich conditions, while NO is the principal nitrogen-containing product in combustion of lean mixtures.

Folsom, et al., performed another series of experiments in which the low-Btu gas was doped with 471 mol ppm NO. The idea was to simulate the second stage of a reheat combustor in which a lean catalytic primary stage is followed by secondary fuel addition and a second

catalytic reactor. Under lean conditions most of the NO passed through the reactor. However, at theoretical air between 60% and 80%, an 80% reduction of the NO was found. No NH_3 or HCN was observed in the exhaust from combustion of the NO doped fuel.

The work described in the present report includes experimental investigations of carbon monoxide and medium-Btu gas combustion in the presence of platinum supported on a monolithic Cordierite substrate. Axial profiles of substrate temperature, gas temperature, and stable species concentrations were measured at different gas velocities and equivalence ratios. The carbon monoxide data were presented in a progress report (Bracco, et al., 1978) and at the Third Workshop on Catalytic Combustion (Walsh, et al., 1979). The medium-Btu gas data were also presented in a progress report (Bracco, et al., 1979). These results were extended by investigation of the catalytic combustion of medium-Btu gases containing hydrogen sulfide (Bracco, et al., 1979) and ammonia, described in Section 5c of this report.

The two-dimensional computer code which is being developed to model catalytic combustion is documented (Section 2), and computed axial and radial gas temperature and carbon monoxide concentration profiles inside a catalyst channel during carbon monoxide combustion are presented in Section 4. The integrated carbon monoxide profiles at the catalyst outlet are compared with the experimentally measured values.

Summaries of the resonance absorption and Raman scattering techniques for measuring gas temperature and species concentrations in combustion systems were prepared, and system concepts for applying these techniques to catalytic combustion were proposed (Bracco, et al., 1979b). A new pulsed multi-pass Raman scattering technique for increasing photon yield from a scattering volume was developed (Santavicca, 1979). A cell and system which maximize the benefits of the technique for combustion diagnostics are described in Section 6b.

2. Two-Dimensional Model*

A steady state computer code, named CATEACH, was developed to predict temperatures, pressures, species mass fractions, and gas velocities in a single channel of a monolithic combustion catalyst. CATEACH is based on the hydrodynamic TEACH code developed at Imperial College (Gosman and Ideriah, 1976), to which energy and species conservation equations, the equation of state, and variable transport properties were added. The model is two-dimensional, axisymmetric, and includes the following physical features:

laminar or turbulent ($k-\epsilon$ model) flows,
axial and radial temperature and pressure-dependent diffusion,
multi-step homogeneous and wall reactions.

The coordinate system and variables describing the gas and substrate are shown below. The governing equations are given in Table 2-1.

* This section based on notes prepared by Y. Yaw. The development of the two-dimensional model is jointly sponsored by the Air Force Office of Scientific Research and under Grant #AFOSR-76-3052, Dr. B. T. Wolfson, Grant Monitor.

Table 2-1. Nondimensional Governing Equations for Reacting Flow in a Circular Tube with Catalytic Wall.

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial \rho v r}{\partial r} + \frac{\partial \rho u}{\partial z} = 0$$

$$\frac{D \rho v}{D t} = - \frac{1}{\gamma_i M_i^2} \frac{\partial p}{\partial r} + \frac{1}{r} \frac{\partial \sigma_{rr} r}{\partial r} + \frac{\partial \sigma_{rz}}{\partial z} + \frac{\sigma_{\phi\phi}}{r}$$

$$\frac{D \rho u}{D t} = - \frac{1}{\gamma_i M_i^2} \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial \sigma_{rz}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z}$$

$$\begin{aligned} \frac{D \rho h}{D t} = & \frac{\gamma_i - 1}{c \gamma_i} \frac{\partial p}{\partial t} + \frac{(\gamma_i - 1)}{c} M_i^2 \frac{1}{r} \frac{\partial}{\partial r} (\sigma_{rr} v r + \sigma_{rz} u r) \\ & + \frac{(\gamma_i - 1)}{c} M_i^2 \frac{\partial}{\partial z} (\sigma_{rz} v + \sigma_{zz} u) - \frac{1}{r} \frac{\partial r q_r}{\partial r} - \frac{\partial q_z}{\partial z} \\ & + D_{II} \rho_1 \rho_2 \exp\left(-\frac{T_A}{T}\right) \end{aligned}$$

$$\begin{aligned} \frac{D \rho_k}{D t} = & \frac{1}{\text{ReSc}} \frac{1}{r} \frac{\partial}{\partial r} \left[\rho D_k r \frac{\partial (\rho_k / \rho)}{\partial r} \right] + \frac{1}{\text{ReSc}} \frac{\partial}{\partial z} \left[\rho D_k \frac{\partial (\rho_k / \rho)}{\partial z} \right] \\ & + W_k (v_k' - v_k'') D_I \rho_1 \rho_2 \exp\left(-\frac{T_A}{T}\right) \end{aligned}$$

$$\rho = \rho T W_i^* \sum (Y_k / W_k)$$

$$\frac{\partial T_w}{\partial t} = \frac{\partial^2 T_w}{\partial z^2} - \frac{2}{s} \frac{k}{k_w} \left(\frac{\partial T}{\partial r} \right)_{R^-} + D_{\text{cat}} \rho_1 \exp\left(-\frac{T_{\text{cat}}}{T_w}\right)$$

The general conservation equation for steady state 2-D flow (axisymmetrical) is:

$$\frac{1}{r} \left[\frac{\partial}{\partial x} (\rho r u \Phi) + \frac{\partial}{\partial r} (\rho r v \Phi) - \frac{\partial}{\partial x} \left(r \Gamma \frac{\partial \Phi}{\partial x} \right) - \frac{\partial}{\partial r} \left(r \Gamma \frac{\partial \Phi}{\partial r} \right) \right] = S_{\Phi}$$

1. $r = 1$ for planar flow
2. In the general equation $\Phi \equiv u, v, k, \epsilon, T, F_k$, etc.
3. $\Phi = 1, \Gamma = S_{\Phi} = 0$ for the continuity equation

For example:

(a) $\Gamma = \mu_{\text{eff}} = \mu_e + \mu_t, S_u = -\partial p / \partial x$ for x-momentum equation

(b) $\Phi = k$, kinetic energy of turbulence: then $\Gamma = \mu_{\text{eff}} / \sigma_k$

$$S_k = G - C_D \rho \epsilon$$

where ϵ = rate of turbulent kinetic energy dissipation

(Launder and Spalding, 1972)

F_k = mass fraction of species k

Method of Solution

General path to predictions:

Volume integration of conservation equations over discretized flow domain yields FDES.

Discretization of flow domain is done according to a staggered grid configuration.

Typical cells are:

Location:

Variable Stored

p, T, k, ϵ

u velocity

v velocity

located on the grid at the boundaries of cells for scalar quantities

Control volume analysis: for the control volume sketched, the conservation equation for ϕ is:

$$\frac{\Delta \rho \phi}{\Delta t} \delta V = \dot{q}_W - \dot{q}_E + \dot{q}_S - \dot{q}_N + S_\phi \delta V$$

i.e., rate of change of ϕ in a cell = net rate of inflow of ϕ to the cell by convective and diffusive fluxes + net rate of generation of ϕ in the cell.

Consider 1-D transport of ϕ across cell boundaries due to convection and diffusion: the "west" flux $\dot{q}_W$ can be written as

$$\dot{q}_W = \rho_W u_W A_W [f_W(\phi_W - \phi_P) + \phi_P]$$

where $f_W = 1$ for pure convection and $f_W \rightarrow \infty$ for pure diffusion.

Approximations made as follows:

$$\frac{\dot{q}_W}{\rho_W A_W u_W} \equiv \begin{cases} 1/2[(1 + 2/Pe_W)\phi_W + (1 - 2/Pe_W)\phi_P] & \text{for } -2 \leq Pe_W \leq 2 \\ \phi_W & \text{for } Pe_W \geq 2 \\ \phi_P & \text{for } Pe_W \leq -2 \end{cases}$$

This method is known as "hybrid differencing" scheme.

$$\frac{1}{2} \left[\left(1 + \frac{2}{Pe_W} \right) \phi_W + \left(1 - \frac{2}{Pe_W} \right) \phi_P \right] = f_W \phi_W + (1 - f_W) \phi_P = \frac{1}{2}(\phi_W + \phi_P) + \frac{1}{Pe_W}(\phi_W - \phi_P)$$

convection diffusion

$$\text{i.e., } f_W = \frac{1}{2} \left(1 + \frac{2}{Pe_W} \right)$$

where $Pe_W =$ Peclet number, $= \rho_W u_W \delta X_{PW} / \Gamma_W$

Sources given by $b\phi_P + c$ where b, c may still be functions of ϕ_P ; substitution into convection law, with the aid of continuity yields:

$$\phi_P = \frac{\sum_i a_i \phi_i + c}{a_P - b} \quad (A-1), \quad \text{with } a_P = \sum_i a_i \quad (i = N, W, S, E)$$

$$a_W = \rho_W u_W A_W f_W, \quad a_S = \rho_S A_S u_S f_S, \text{ etc. ----}$$

Boundary conditions:

1. Grid constructed so that boundaries coincide with control volume (cell) walls.
2. In $\dot{q}_W - \dot{q}_E + \dot{q}_S - \dot{q}_N + S_\phi \delta V = 0$,

appropriate flux or boundary value must be given to $\dot{q}_W$. In the finite difference expression this is equivalent to:

- (a) Breaking P-W link by setting $a_W = 0$.

(b) Inserting correct flux via "false" source.

Boundary flux, $\dot{q}_B$, prescribed: in

$$\phi_P = \frac{\sum_i a_i \phi_i + c}{a_P - b} \quad \text{set} \quad \begin{cases} a_W = 0 \\ b = 0 \\ c = \dot{q}_B \end{cases}$$

Boundary value, ϕ_B , prescribed.

$$\text{set} \quad \begin{cases} \dot{q}_W = a_W(\phi_B - \phi_P), \\ \text{so that} \quad \begin{cases} a_W = 0 \\ b = -a_W \\ c = a_W \phi_B \end{cases} \end{cases}$$

To set ϕ_P at any internal node to a value ϕ_{fix}
 set $b = -10^{30}$ $c = 10^{30} \phi_{fix}$

Tri-Diagonal Matrix Algorithm for solution of Equation (A-1)

The FDE is:

$$\phi_P = \frac{\sum_i a_i \phi_i + c}{a_P - b} \quad \text{or}$$

$$-a_S \phi_S + (a_P - b) \phi_P - a_N \phi_N = a_W \phi_W + a_E \phi_E + c$$

Let $a_W \phi_W + a_E \phi_E + c = c'$ → known from previous iteration.

For $J = 2$ to $J = NJ - 1$:

$$-B_2 \phi_1 + D_2 \phi_2 - \alpha_2 \phi_3 = c'_2$$

$$-B_3 \phi_2 + D_3 \phi_3 - \alpha_3 \phi_4 = c'_3$$

$$-B_J \phi_{J-1} + D_J \phi_J - \alpha_J \phi_{J+1} = c'_J$$

$$B_n \phi_{n-1} + D_n \phi_n - \alpha_n \phi_{n+1} = c'_n$$

all B , α , D , c' , and ϕ_1 and ϕ_{n+1} are known quantities.

Tridiagonal matrix algorithm allows the previous system to be solved from recurrence formula:

$$\phi_j = A_j \phi_{j+1} + c'_j \quad \text{With } A_j = \alpha_j / (D_j - B_j A_{j-1})$$

$$c_j = (B_j c'_{j-1} + c'_j) / (D_j - B_j A_{j-1}) \quad A_1 = 0, c'_1 = \phi_1$$

Each line is "traversed".

The whole grid is "swept".

SIMPLE

Semi-implicit method for pressure linked equations.

All variables except pressure satisfy a conservation equation.

Define

$$p = p^* + p', \quad G = G^* + G' \quad (\text{mass fluxes per unit area}),$$

$$u = u^* + u', \quad v = v^* + v', \quad \text{with:}$$

* (values found from p^*)

' (corrections to values found from p^*)

The objective is to find p' and u' in order to correctly obtain p and u fields.

Using a linearized flux relation, G' can be found as:

$$G'_W = \rho^* \frac{\partial u_W^*}{\partial (p_W^* - p_P^*)} (p'_W - p'_P)$$

From momentum equation:

$$D_W = \frac{\partial u_W^*}{\partial (p_W^* - p_P^*)} = \frac{A_{EW}}{a_P - b}$$

$$\text{Hence, } G'_W = \rho^* D_W (p'_W - p'_P)$$

Mass conservation implies:

$$G_E A_E - G_W A_W + G_N A_N - G_S A_S = \underbrace{S_m \delta V}_{\neq 0} \quad \text{when velocity does not satisfy continuity.}$$

Substitute $G_W = G_W^* + G_W'$ etc. --- into continuity equation to obtain the pressure correction equation.

$$a_P p_P' = \sum_i a_i p_i' + M_P \quad a_P = \sum_i a_i \quad a_W = \rho_W D_W A_W$$

$$M_P = G_W^* A_W - G_E^* A_E + G_S^* A_S - G_N^* A_N = \text{Residual Mass}$$

Knowing p' allows updating G^* and u^* to G and u .

Boundary conditions:

- (i) Normal velocity to the boundary. Set $A_N = 0$
- (ii) Pressure at boundary prescribed. Set $p' = 0$.

Chemical Reaction (Propane taken as example):

- (a) for simplicity we illustrate the case of infinitely fast reaction at wall, and semi-global mechanism for propane oxidation in the gas phase:

Species #: 1 2 6 3 4

5

- (b) Rate equation:

$$\frac{d[C_3H_8]}{dt} = -4.97[C_3H_8]^{1/2} \exp(-9195/RT) \text{ mole/cm}^3 \text{ sec}$$

$$\frac{d[CO]}{dt} = -1.3 \times 10^{14} [CO][O_2]^{1/2} [H_2O]^{1/2} \exp(-30000/RT) \text{ mole/cm}^3 \text{ sec}$$

(Howard, Williams, and Fine, 1973)

(c) $F_{C_3H_8} = F_{CO} = 0$ at wall (infinitely fast reaction at wall)

(d) Put $A_N = 0$ to make the flux to the wall zero, and transfer this flux into the source term.

Surface reactions: Details:

$$\begin{aligned} \text{Diffusion flux at } C_3H_8 \text{ to the wall: } -D_1 A \frac{\partial F_1}{\partial y} &= -D_1 A (F_{1W} - F_{1P})/Y_P \\ &= D_1 A F_{1P}/Y_P \quad (A = \text{area}) \end{aligned}$$

$$= -D_1 A (DY1DR) \quad (\text{in computer program: } DY1DR = -F_{1P}/Y_P)$$

$$\begin{aligned} \text{Similarly, diffusion flux of } CO \text{ to the wall: } -D_3 A \frac{\partial F_3}{\partial y} &= \\ &= D_3 A F_{3P}/Y_P = -D_3 A (DY3DR) \quad (\text{in computer program: } DY3DR = -F_{3P}/Y_P) \end{aligned}$$

At the wall, two infinitely fast reactions occur:

1. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
2. $CO + \frac{1}{2}O_2 \rightarrow CO_2$

From this we know that there must be stoichiometric amount of

1. O_2 : the flux diffuses to the wall and reacts infinitely fast with C_3H_8 and CO , $= -5D_1 A (DY1DR) - 5D_3 A (DY3DR)$
2. CO_2 flux produced at wall:
 $= 3D_1 A (DY1DR) + D_3 A (DY3DR)$
3. H_2O flux produced at wall:
 $= 4D_1 A (DY1DR)$

Gas phase reactions: Details:

Two Reactions:

$$1. \frac{d[C_3H_8]}{dt} = -4.97[C_3H_8]^{1/2} \exp(-9195/RT) \text{ mole/cm}^3 \text{ sec}$$

$$2. \frac{d[CO]}{dt} = -1.3 \times 10^{14} [CO][O_2]^{1/2} [H_2O]^{1/2} \exp(-30000/RT) \text{ mole/sec}$$

In the computer program: $OMEDOT(1) = -d[C_3H_8]/dt$

$OMEDOT(2) = -d[CO]/dt$

Put mass production per unit time into source:

In the computer program:

RODOTK = 0.

DO 170 L = 1, NR (NR = # of reactions)

RODOTK = RODOTK + W(K)*(B(K,L) - A(K,L))* OMEDOT(L)

170 CONTINUE

where:

$W(K)$ = molecular weight of species k

$B(K,L)$ = backward reaction stoichiometric coefficient of species k in reaction #L.

$A(K,L)$ = forward reaction stoichiometric coefficient of species k in reaction #L.

3. The heat released by chemical reaction must be put into the source term in CALCT (the subroutine which calculates the temperature field).

In the computer program:

QDOT = 0.

DO 120

120 QDOT = QDOT + Q(L)*OMEDOT(L)

Q(L): heat release per unit fuel mass for reaction L.

Transfer QDOT into mass production term: $QDOT \cdot \delta V / c_p \cdot T = QDOTV$

Outline of Complete Solution Procedure

1. Guess or estimate initial variable fields.
2. Assemble coefficients of momentum equations solved for u^* and v^* , LBL procedure, using previous p^* field.
3. Obtain coefficients and mass sources for p' equation. Solve for p' , LBL procedure. Find u' , v' velocities $[u'_W = \rho D_W (p'_W - p'_p)]$.
4. Update p , u , v according to: $p = p^* + p'$, $u = u^* + u'$, $v = v^* + v'$.
5. Assemble coefficients and solve equations for remaining variables, k , ϵ , T --- etc., using LBL procedure.
6. Test for convergence -- if not satisfactory repeat 2-6 using latest values as initial guess.

Convergence

1. Convergence will always exist in iterative solution of

$$\phi_p = \frac{\sum_i a_i \phi_i + c}{a_p - b}$$

when $|a_p - b| \leq \sum_i |a_i|$ for which $b \leq 0$ is required.

2. Test for convergence based on calculation of residual sources defined as:

$$R_\phi = (a_p - b)\phi_p - (\sum_i a_i \phi_i + c). \quad \text{It is required that}$$

$$\sum |R_\phi| < \lambda R_{\phi \text{ref}}, \quad \lambda \approx 10^{-3} \text{ (typical)}.$$

Under-relaxation

Required because of the non-linearities in the FDE's:

$$\phi^{\text{taken}} = f\phi^{\text{new}} + (1-f)\phi^{\text{old}}, \quad \text{where } 0 \leq f \leq 1, \text{ usually around } .5.$$

Accuracy depends on:

1. Degree to which solution satisfies FDE's (examine R_ϕ 's).
2. Degree to which FDE solution satisfies PDE's (refine grid).
3. Location of, and conditions imposed at, boundaries.
4. Adequacy of the turbulence model (compare with experiment).

STRUCTURE OF COMPUTER CODE

SUBROUTINES:

CONTRO - sequencing, overall control, initial and final operations, iteration control.

INIT - grid geometry

PROPS - fluid properties.

PRINT - output of calculated arrays.

CALC ϕ - calculation of ϕ .

LISOLV - LBL iteration.

PROMOD - sources and BCs.

GENERAL STRUCTURE OF CALC ϕ

Small difference when $\phi = p$ for CALC ϕ

Note: Coefficients are updated each iteration; the ϕ 's every traverse within a sweep. There can be several sweeps per iteration, usually 3 to 5.

Nomenclature for Section 2

A	frequency factor for homogeneous reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$
A_{cat}	frequency factor for wall reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$
c	$= h_i / C_{p_i} T_i$
C_p	specific heat at constant pressure, $\text{J/kg}\cdot\text{K}$
D	diffusion coefficient, m^2/s
D_{cat}	$= 2\rho_i Q_{\text{cat}} A_{\text{cat}} L^2 / k_w T_i s$
D_I	Damköhler number of the first kind $= L\rho_i A / u_i W_1 W_2$
D_{II}	Damköhler number of the second kind $= Q L\rho_i A / h_i u_i W_1 W_2$
E_A	activation energy for homogeneous reaction, J/kmol
E_{cat}	activation energy for wall reaction, J/kmol
h	nondimensional enthalpy $= \tilde{h} / h_i$
k	thermal conductivity of gas, $\text{J/m}\cdot\text{s}\cdot\text{K}$
k_w	thermal conductivity of wall, $\text{J/m}\cdot\text{s}\cdot\text{K}$
L	catalyst length, m
M	Mach number
p	nondimensional pressure $= \tilde{p} / p_i$
q_r, q_z	nondimensional components of heat flux $= \tilde{q}_r / \rho_i u_i h_i, \tilde{q}_z / \rho_i u_i h_i$
Q	heat of homogeneous reaction, J/kg
Q_{cat}	heat of wall reaction, J/kg
r	nondimensional radial coordinate $= \tilde{r} / L$
R	gas constant $= 8314 \text{ J/K}\cdot\text{kmol}$; nondimensional pipe radius $= \tilde{R} / L$
Re	Reynolds number
s	thickness of catalyst substrate, m
Sc	Schmidt number
t	nondimensional time $= \tilde{t} u_i / L$
T	nondimensional temperature $= \tilde{T} / T_i$
T_A	nondimensional characteristic temperature for homogeneous reaction $= E_A / RT_i$
T_{cat}	nondimensional characteristic temperature for wall reaction $= E_{\text{cat}} / RT_i$
u	nondimensional axial component of velocity $= \tilde{u} / u_i$
v	nondimensional radial component of velocity $= \tilde{v} / u_i$

W molecular weight, kg/kmol
 W^* $= 1/\sum(Y_k/W_k)$, kg/kmol
 x axial coordinate, m
 X mole fraction
 Y mass fraction
 z nondimensional axial coordinate $= \tilde{z}/L$
 γ ratio of specific heat at constant pressure to specific heat at constant volume
 ν stoichiometric coefficient
 ρ nondimensional density $= \tilde{\rho}/\rho_i$
 $\sigma_{rr}, \sigma_{\phi\phi}, \sigma_{zz}, \sigma_{rz}$ nondimensional components of viscous stress tensor
 $= \tilde{\sigma}_{rr}/\rho_i C_{p_i} T_i (\gamma_i - 1) M_i^2$, etc.
 ϕ equivalence ratio

Subscripts

i inlet
 k species index
 r reference
 w wall
 1 fuel
 2 oxidizer

Superscripts

$'$ reactant
 $''$ product
 $-$ gas side of gas/solid interface
 $\sim$ dimensional variable

3. Experimental Apparatus

Substrate temperatures and exhaust gas compositions and temperatures were measured during lean, premixed combustion of carbon monoxide and a medium-Btu gas in a monolithic catalyst. The measurements were made using the flow reactor shown schematically in Figure 3-1. Preheated oxidizer is supplied to a 700 mm long test section having a 25.4 mm square duct. A monolithic "honeycomb" catalyst is placed with its downstream end 90 mm from the test section outlet, and insulated from the wall by Fiberfrax paper. A fuel injection grid such as that shown in Figure 3-2, consisting of five 1.6 mm diameter tubes, each containing four or five holes, is located 440 mm from the catalyst inlet. A flowmeter (Hastings Model AHL-100P with H-3M/L-100 transducer) was used to measure the mass flowrate of air or nitrogen. Pressure was regulated by a valve in the exhaust pipe, and taps placed up and downstream of the catalyst were used to measure reference pressure and pressure drop. A combination pitot-static and thermocouple probe was used to measure reference velocity and gas temperature, and also to extract gas samples. The probe could traverse the inlet stream to determine radial uniformity of temperature, velocity, and fuel concentration. A continuous effort was made to improve the radial uniformity of the reference conditions. The entire test section was insulated so that uniform temperature across the inlet stream was obtained when sufficient time (about 1 hour) had elapsed after startup of the oxidizer preheat system. In the CO experiments baffles were used to promote mixing of the fuel and air, but they were not used for the medium-Btu gas. More details concerning the uniformity of gas properties upstream of the reactor; and some typical radial profiles of inlet gas temperature, composition, and velocity are presented in Appendix A.

Substrate temperatures were measured by a method similar to that described by Kesselring, Krill, and Kendall (1977). Ni-Cr/Ni-Al thermocouples were fed through the test section wall and into the ends of catalyst channels. The lengths of wire inside the catalyst were covered by mullite insulator and both ends of the channel were sealed with ceramic adhesive. A radial temperature distribution in the substrate was measured at the axial position of highest substrate temperature, to determine the effect of heat conduction to the wall of the test section. The measured profile is shown in Figure 3-3. The variation of substrate temperature at this axial position was ± 20 K over 45% of the sample width.

An expansion quenched, water cooled, stainless steel gas sampling probe was mounted through an elbow in the exhaust pipe and could be moved along the axis of the test section. Exhaust gas temperatures were measured using a thermocouple mounted in the same way as the gas sampling probe, or on the probe itself. Because the exhaust is an important component of the overall system, in which further reactions may take place, the axial dependences of the gas temperature and species

concentrations were measured by moving the thermocouple/sampling probe downstream from the catalyst outlet. Details of the catalyst and probe arrangement are shown in Figure 3-4. Flashback arrestors were placed upstream of the catalyst for the medium-Btu gas experiments because fuel concentrations were expected to exceed the lean flammability limit.

CO and CO₂ were determined by infrared absorption (Horiba Model AIA-21). In the CO experiments, O₂ was determined by magnetic susceptibility (Scott Model 250). In the medium-Btu gas experiments H₂, O₂, and CH₄ were separated by gas chromatography (Hewlett-Packard 5830A) on a 6' x 1/8" column packed with molecular sieve 5A, using N₂ carrier gas. H₂ and O₂ were then detected by thermal conductivity, and CH₄ by flame ionization. The water content of the inlet air was measured using a semiconductor sensor (Thunder Model 2000 with BR-101B probe) mounted in the air stream between the receiving tank and heaters. A chart of the air, inert gas, oxygen, fuel, fuel dopant, and sample flows is shown in Figure 3-5.

The catalyst was platinum supported on split-cell corrugated Cordierite with γ -alumina washcoat. The approximate dimensions of the monolith were 24 x 24 x 76 mm, its open area was 64%, and the cross-sectional area of a single channel was 1.9 mm². The physical properties of the monolith are listed in Table 3-1.

The performance of a particular catalyst/fuel system is examined by systematic variation of equivalence ratio, inlet temperature, and gas velocity; with measurement of substrate temperatures, exhaust gas temperature, and exhaust gas composition at each set of conditions.

Table 3-1. Catalyst Properties

SUBSTRATE: Cordierite, American Lava Corp., AlSiMag 795, split cell

length 0.0760 ± 0.0003 m
wall thickness 0.25×10^{-3} m
open area 64%
channels per unit area 0.34×10^6 m⁻²
open area per channel 1.9×10^{-6} m²
ratio surface area to total volume 2100 m²/m³
ratio surface area to gas volume 3260 m²/m³
channel hydraulic diameter (4/3260) 0.00123 m
bulk density 610 kg/m³
solid density 1700 kg/m³
safe operating temperature 1473 K
specific heat 800 J/kg·K
coefficient of thermal expansion (linear, 294 - 1033 K) 3.8×10^{-6} K⁻¹
thermal conductivity of solid (572 K) 1.4 J/m·s·K
approximate channel cross-section is a trapezoid with base lengths .0011 m and .0023 m, and height .0012 m

WASHCOAT: γ -alumina

loading 115 - 125 kg/m³
surface area (BET) $(29.2 - 33.0) \times 10^6$ m²/m³

CATALYST: platinum

loading 4.2 kg/m³
surface area (CO chemisorption) 6×10^4 m²/m³

The γ -alumina and platinum were applied by Matthey Bishop, Inc., Malvern, PA.

4. Experimental and Theoretical Results on Catalytic Oxidation of Carbon Monoxide

4a. Experimental Results

The conditions at which CO/air combustion in Pt/ γ -Al₂O₃/Cordierite was studied are listed in Table 4-1. The reactor was operated over a range of equivalence ratios and reference velocities at fixed reference temperature and pressure. The fuel was carbon monoxide, 99.5 mole %.

Catalysts were pretreated to stabilize surface area and platinum concentration by running for several hours at maximum substrate temperatures approximately 100 K higher than those at which exhaust temperature and composition measurements were made. The present data were obtained using two samples whose dimensions and pretreatment are summarized below.

Sample #8: 24.6 x 24.6 x 76.0 $\pm$ 0.3 mm

Pretreatment: 2.3 hr with propane at maximum substrate temperature 1510 $\pm$ 20 K.

Total run time: 9 hr

Sample #10: 24.1 x 24.1 x 76.0 $\pm$ 0.3 mm

Pretreatment: 3.1 hr with propane and 2.1 hr with CO at maximum substrate temperature 1470 $\pm$ 20 K.

Total run time: 22 hr

Natural propane, 96 mol %, was the fuel used for pretreatment. In selecting the operating conditions, no attempt was made to minimize unburned fuel, rather the objective was to begin determination of the relationships between these conditions and performance characteristics.

Figures 4-1 and 4-2 show substrate temperature, exhaust temperature, and exhaust composition as functions of axial position, obtained at three equivalence ratios with fixed reference velocity. The substrate and gas temperatures increased with increasing equivalence ratio, as expected. Unburned CO was consumed by homogeneous reaction in the exhaust at a rate which increased with increasing average exhaust gas temperature. Gas temperature increased with distance downstream due to heat release from the reaction. The amount of unburned CO at the catalyst outlet was practically independent of inlet equivalence ratio. In a purely mass transfer limited regime, unburned CO is expected to increase with increasing equivalence ratio. On the other hand, if conversion is dominated by homogeneous reaction, unburned CO should decrease as equivalence ratio increases. Under the operating conditions of Figures 4-1 and 4-2, the system was apparently in an intermediate regime. The substrate temperatures in Figure 4-1 show a relative maximum at a distance 15-20 mm from the inlet. This may be an

Table 4-1. CO/Air Combustion in
Pt/ γ -Al₂O₃/Cordierite Catalyst

Run No.	P _o (kPa)	T _o (K)	ϕ	u _o (m/s)	H ₂ O (mol%)	$\Delta P/P_o$ (%)	T _{ad} (K)
8-1	105	700	.22	22	1.4	5.5	1430
8-2	109	700	.23	30	1.2	8.4	1450
8-3	109	700	.23	21	1.2	5.4	1450
8-4	109	700	.24	15	1.2	3.5	1460
8-5	109	700	.27	31	1.1	8.8	1540
8-6	109	700	.24	30	1.4	8.0	1470
10-3	112	700	.26	31	1.8	8.6	1520
10-4	112	700	.24	19	3.0	4.6	1480
10-5	112	700	.27	19	3.0	4.8	1550
10-6	112	700	.30	19	3.0	5.0	1630
10-7	112	700	.15	6	3.7	1.0	1200
10-8	112	700	.19	5	3.7	1.1	1330
10-9	112	700	.23	5	3.6	1.2	1440
10-10	112	700	.23	5	3.2	1.2	1440
10-11	112	700	.24	6	2.0	1.2	1470
10-12	112	700	.27	11	1.6	2.4	1540
10-13	112	700	.28	20	1.5	4.3	1580

example of the effect explained by Pfefferle (1978) as resulting from heat recirculation from the catalyst to the inlet gas stream.

Figures 4-3 to 4-6 show data obtained at various reference velocities with fixed equivalence ratio. The line representing the substrate temperature of Figure 4-3 is reproduced in Figures 4-4 and 4-5 to show the similarity of the data points. Substrate temperature did not exhibit a sensitive dependence on gas velocity, consistent with the concept that in a system with mass transfer limited surface reaction rate, the substrate temperature depends, in a first approximation, only on the adiabatic reaction temperature. Exhaust composition is shown in Figure 4-6. The concentrations of O_2 and CO_2 were nearly the same for the three runs, but unburned CO increased with increasing reference velocity.

Figure 4-7 shows the ratio of unburned CO to inlet CO as a function of reference velocity for the entire series of runs. The amount of unburned CO was obtained by extrapolating to the catalyst outlet. This figure combines data taken at various equivalence ratios and H_2O concentrations. The dependence of pressure drop on reference velocity is shown in Figure 4-8.

Rate coefficients for CO oxidation in the exhaust were estimated from the slopes of the lines on the plots of $\log X_{CO}$ vs. z . The assumed rate expression for homogeneous CO oxidation was taken from Howard, Williams, and Fine (1973):

$$\frac{dC_{CO}}{dt} = -A C_{CO} C_{O_2}^{1/2} C_{H_2O}^{1/2} \exp(-E_a/R_o T)$$

An average measured exhaust temperature was used to determine average exhaust velocity and density. O_2 concentration in the exhaust was assumed constant, and the H_2O concentration was estimated from the measurement in the inlet air. An Arrhenius plot of the calculated rate coefficients, $A \exp(-E_a/R_o T)$, is shown in Figure 4-9. The solid line is the fit by Howard, et al. (1973) to a large number of homogeneous CO oxidation data over the range 840-2360 K:

$$A = 1.3 \times 10^{14} \text{ cm}^3/\text{mol} \cdot \text{s}$$

$$E_a = 126 \text{ kJ/mol}$$

The agreement of the rate coefficients derived from the present data with those from the primarily homogenous systems indicates that the oxidation of CO in the exhaust is not drastically changed under these conditions by the presence of the catalytic reactor upstream.

4b. Comparison of Computed and Measured Carbon Monoxide Data

The test of the model described in Section 2 is in the agreement of its predictions with observations such as those presented in Section 4a. Earlier stages in the development of the model were described in Progress Reports (Bracco, et al., 1979a, and 1979b). It was shown that the measured CO emissions versus reference velocity could be reproduced by assuming that the surface reaction rate is infinitely fast and simultaneously reducing the diffusion coefficients by a factor of 4. Since the surface temperature is a weak function of the reference velocity, this was a clear indication that surface reactions are not infinitely fast. Therefore attention was focused on incorporating in the model an expression for the oxidation rate of CO on platinum.

Shishu (1972) gives several expressions for CO oxidation rates on platinum depending on temperature and mechanism proposed for oxidation. The most general expression may be written as

$$\dot{C}_{CO} = - \frac{\sigma_{Pt}^k K_{CO}^a K_{O_2}^b p_{CO}^c p_{O_2}^d}{\{1 + (K_{CO} p_{CO})^e + (K_{O_2} p_{O_2})^f\}^g} \quad \text{kg/m}^2 \cdot \text{s} \quad (4-1)$$

Where σ_{Pt} is the platinum area coverage, i.e., kg of Pt/unit area. K_{CO} and K_{O_2} are equilibrium constants for chemisorption of CO and O_2 on platinum, p are partial pressures, and a, b, c, c, e, f, g are exponents that depend on the particular mechanism assumed to control the oxidation. The term downstairs is in effect representing the influence of chemisorption. There is evidence (Voltz et al., 1973; Carberry, 1976) that at low temperatures (~ 600 K) the rate is inversely proportional to CO concentration, i.e., $c = 1$ and $e \cdot g = 2$. At higher temperatures the rate should become progressively independent of chemisorption. In the absence of conclusive data, a simple expression for the rate, of the form

$$\dot{C}_{CO} \sim - A_s C_{CO} \exp(-E_{a,s}/R_o T) \quad (4-2)$$

was used. The activation energy was chosen (from Voltz) as 24.9 kcal/mol, and A_s was varied until a good match between experimental data and predictions was obtained. It should be noted that A_s includes implicitly the dependence on σ_{Pt} . Since the platinum coverage is a badly known quantity, and varies with time as the catalyst ages, this procedure is the most sensible to yield a reasonable model. The value of A_s was chosen to match CO emissions for the reference velocity $u_o = 30$ m/s and equivalence ratio $\phi = .24$. The value obtained was $A_s = 3.82 \times 10^3$ m/s. This value was subsequently used to reproduce other experimental runs with different velocities and equivalence ratios.

Figures 4-10 to 4-13 show computed radial and axial temperature and CO concentration profiles for two cases: $u_0 = 30$ m/s, $\phi = .24$ and $u_0 = 5$ m/s, $\phi = .19$. At the higher speed, gradients persist for a much longer distance along the channel than for the lower velocity case. This points out the necessity of using a 2-dimensional description of the physics and chemistry of catalytic combustion.

Values for comparison with the experimental results are found by integrating radial profiles such as those in Figures 4-10 and 4-12. The predicted gas temperatures and compositions at the reactor outlet for a range of reference velocities are shown with the experimental data in Figures 4-3 to 4-6. The predicted dependence of the fraction of CO unburned on reference velocity is in excellent agreement with the experimental data for $\phi = .19-.30$ as shown in Figure 4-7. The predicted pressure drop also compares well with the observations (Figure 4-8). One source of disagreement between predicted and observed values is probably the trapezoidal cross-section of the monolith channels, which is approximated in the model by a circle.

NOMENCLATURE FOR SECTION 4

a,b,c,....	= reaction order exponents
A	= pre-exponential factor
C_k	= concentration of species k, kmol/m ³
C_p	= specific heat at constant pressure, J/K-kg
D_k	= diffusion coefficient of species k in nitrogen, m ² /s
E_a	= activation energy, J/kmol
k	= rate coefficient = $A \exp (-E_a/R_0 T)$
K_k	= equilibrium constant for chemisorption of species k on platinum
L	= length of catalyst, m
Le_k	= Lewis number of species k = $\lambda/\rho D_k C_p$
p_k	= partial pressure of species k, Pa
p	= pressure, Pa
r	= radial coordinate, m
R	= radius of catalyst channel, m
R_0	= gas constant = 8314 J/K-kmol
Re	= Reynolds number
t	= time, s
T	= temperature, K
u	= velocity, m/s
z	= axial coordinate, m
X_k	= mole fraction of species k
Y_k	= mass fraction of species k
λ	= thermal conductivity, J/m-s-K
ρ	= density, kg/m ³

σ_{Pt} = surface coverage, kg Pt/m²

ϕ = equivalence ratio

$\langle \cdot \rangle$ = average value

Subscripts

ad = adiabatic

k = species index

4 = axial position corresponding to the catalyst outlet

0 = reference

s = catalyst substrate or surface

Superscripts

• = differentiation with respect to time

5. Experimental Results on Medium-Btu Gas/Air

5a. Medium-Btu Gas Having Negligible Sulfur and Nitrogen-Containing Impurities

The medium-Btu gas was supplied by Matheson Gas Products (certified gas mixture). The five cylinders used had the following range of compositions:

H ₂	.400 - .404 (mole fraction)
CO	.193 - .198
CH ₄	.102 - .105
CO ₂	.294 - .305

A 26 mm long section of DuPont Torvex honeycomb with 1 mm diameter channels was placed upstream of the catalyst with a gap of 1.5 mm between. This was intended to act as a flashback arrestor, and no flashback occurred during the experiments. CO and CO₂ were determined by infrared absorption. H₂, O₂, and CH₄ were separated by gas chromatography on a 6' x 1/8" column packed with molecular sieve 5A, using N₂ carrier. H₂ and O₂ were detected by thermal conductivity, and CH₄ by flame ionization. Pressure taps were located in the inlet stream, between the flashback arrestor and catalyst, and in the exhaust. The pressure drop across the flashback arrestor was at most 2 kPa.

Medium-Btu gas/air combustion in the Pt/γ-Al₂O₃/Cordierite catalyst was investigated for the following reference conditions:

Reference temperature,	T ₀ = 400, 590 K
Reference pressure,	P ₀ = 120 kPa
Average reference velocity,	<u ₀ > = 5-24 m/s
Reference mole fraction fuel,	(X _{H₂} + X _{CO} + X _{CH₄} + X _{CO₂}) ₀ = 0.06-0.15

The reference conditions, catalyst pressure drop, and adiabatic temperature for each run are presented in Table 5-1. The average gas velocity, <u₂>, immediately after entering the catalyst; taking into account the ratio of catalyst geometric area to duct area and the fraction of catalyst open area; is related to the average reference velocity, <u₀>, by:

$$<u_2> = (1.8 \pm .1) <u_0>$$

Table 5-1. Reference Conditions, Catalyst Pressure Drop, and Adiabatic Temperature for the Medium-Btu Gas Runs.

Run #	P ₀ (kPa)	T ₀ (K)	(x _{fuel}) ₀	<u ₀ > (m/s)	(x _{H₂O}) ₀	ΔP/P ₁ (%)	T _{ad} (K)
12-1	120	400	.122	9.8	.005	3.6	1280
12-2	120	400	.122	19.4	.005	8.6	1280
12-3	120	400	.122	4.8	.005	1.5	1280
12-4	120	400	.122	24.5	.005	12.0	1280
12-5	120	400	.122	9.8	.005	3.3	1280
12-6	120	400	.059	4.5	.006	0.6	850
12-7	120	400	.092	4.7	.006	0.9	1090
12-8	120	400	.154	5.0	.007	1.9	1490
12-9	120	400	.122	4.8	.006	1.3	1280
12-10	120	590±11	.122	7.1	.008	1.7	1450

Notes

1. Average fuel composition:

$$x_{H_2} = 0.403 \pm 0.003$$

$$x_{CO} = 0.196 \pm 0.003$$

$$x_{CH_4} = 0.104 \pm 0.002$$

$$x_{CO_2} = 0.297 \pm 0.008$$

2. <u₀> is the average gas velocity calculated from air flow rate and fuel mole fraction.

3. P₁ is the static pressure in the space between the flashback arrestor and the catalyst inlet. (P₀ - P₁) ≤ 2 kPa

Axial profiles of substrate and exhaust gas temperatures at different reference velocities (runs 12-1 through 12-5) are shown in Figure 5-1. The initial and final runs of the series were made at identical reference conditions to give an indication of the reproducibility of the temperature measurements. The substrate temperature profiles are complicated by the presence of three different fuel components: H_2 , CO, and CH_4 , having Lewis numbers ($Le_k = \lambda / \rho D_k C_p$) less than, equal to, and greater than one, respectively (Pfefferle, 1978). A composition profile of the exhaust which is typical of these runs is shown in Figure 5-2. The exhaust gas temperatures in all cases were so low that little, if any, reaction occurred in the exhaust. The fractions of unburned fuel species at the catalyst exit are shown as functions of reference velocity in Figure 5-3. These values were determined by extrapolating the observed mole fractions back to the position of the catalyst exit (1 mm upstream of the first measurement), and dividing by the reference mole fraction of each component. The unburned fraction increases with increasing reference velocity for all three species. Duplicate runs were made at 5 and 10 m/s. The conversion of CH_4 is significantly poorer at the later times (upper points) indicating that the conditions were marginal for CH_4 oxidation.

Four different fuel mole fractions were used (runs 12-3 and 12-6 through 12-9). During this series, the mass flowrate of air was kept fixed, therefore the reference velocity increases slightly with increasing fuel concentration (see Table 5-1). The composition profile for the highest fuel concentration is shown in Figure 5-4. This was the only run of this set for which the exhaust temperature was high enough that significant changes in composition occurred downstream of the catalyst. Near the outlet one actually observes increases in CO and H_2 which are being formed in reactions of CH_4 .

A single run was made with a reference temperature of 590 K. Exhaust reactions were also observed in this case as shown in Figure 5-5.

The fractions of unburned CO and CH_4 at the catalyst exit are shown as functions of adiabatic reaction temperature in Figure 5-6. At the lowest adiabatic temperature, CH_4 oxidation was not detectable. However at the highest temperature, unburned CH_4 at the exit is less than 300 mole ppm. CO conversion improves slightly over the range of adiabatic temperatures studied.

Rate coefficients for CO oxidation were calculated from the slopes of $\log X_{CO}$ versus distance (lines drawn in Figures 5-4 and 5-5), assuming constant exhaust temperature, velocity, and H_2O and O_2 concentrations. The rate expression obtained by Dryer and Glassman (1973) and by Kozlov (1959) was used:

$$\frac{dC_{CO}}{dt} = - C_{CO} C_{O_2}^{\frac{1}{2}} C_{H_2O}^{\frac{1}{2}} A \exp(-E_a/R_o T)$$

The calculated rate coefficients are shown in Figure 5-7 with the values obtained in the experiments on CO combustion. Rate coefficients obtained from CO measurements in the exhaust from catalytic combustion of C_3H_8 are also included. The C_3H_8 data are shown in Appendix B. The relative values of the rate coefficients for the three fuels are consistent with the observation by Dryer and Glassman (1973) that CO oxidation is slower in the presence than in the absence of hydrocarbon.

5b. Effects of Hydrogen Sulfide

Runs were made using a medium-Btu gas doped with H_2S to assess the effect of fuel sulfur on the catalytic reactor's performance. The reference, catalyst, and outlet conditions for these runs are given in Table 5-2, with data for corresponding runs in which H_2S was not present. The flow rate of H_2S was determined from the pressures upstream and downstream of a metering valve having a known flow coefficient.

Two series of experiments were performed:

- (1) Variation of H_2S concentration with other conditions fixed.
- (2) Variation of equivalence ratio with H_2S concentration and other conditions fixed.

Figure 5-8 shows the effects on substrate temperature of varying amounts of H_2S in the fuel. Substrate temperatures at axial positions 10 and 70 mm from the catalyst inlet are given for a range of H_2S mole fractions in the fuel from 0 to 1.8%. Numbers adjacent to the experimental points indicate the order in which the measurements were made. It is apparent from the figure that the presence of H_2S causes a decrease in substrate temperature at both axial positions, particularly near the inlet. However, it is important to note that combustor operation is maintained, even at the highest H_2S concentration. With removal of the H_2S the catalyst always returns to the same temperature profile, indicating that the major effects of H_2S on the catalyst are reversible. There appears to be a hysteresis effect when the H_2S concentration is first increased and then decreased (points numbered 3-9). If two catalyst states are possible over some range of H_2S concentration, the lower temperature state may correspond to heating of the catalyst primarily by heat transfer from a flame in the exhaust. This point needs to be investigated further.

Figures 5-9 to 5-11 show the effects on emission of the fuel components as H_2S concentration is varied. For these measurements the gas sampling probe was positioned 1 mm from the downstream face of the catalyst. This distance corresponds to a time of 0.03 - 0.07 ms, depending on the average gas temperature at the catalyst outlet. The fraction of fuel unconverted increases as H_2S concentration increases except in the case of CH_4 (Figure 5-11) where the scatter of the data is such that a significant trend cannot be distinguished. The hysteresis is especially apparent in the case of unburned H_2 (Figure 5-9). Conversion of each component returns to approximately the same value when H_2S is removed from the fuel.

The data obtained when varying the equivalence ratio (adiabatic temperature) keeping H_2S fixed are shown in Figures 5-12 to 5-15. The maximum substrate temperatures with and without H_2S are similar, although the axial positions of the maxima are different. Conversions of H_2 and CO are poorer when H_2S is present for the three equivalence ratios studied, but their reactions are not extinguished.

Table 5-2. Reference, Catalyst, and Outlet Conditions for Runs Using Hydrogen Sulfide Doped Medium-Btu Gas.

Run #	$(X_{\text{fuel}})_o$	$X_{\text{H}_2\text{S}}$ in fuel	$\Delta P/P_o$ (%)	T_{ad} (K)	T_s $z=1$ mm (K)	T_s $z=5$ mm (K)	T_s $z=10$ mm (K)
12-13	.103	0	2.6	1340	935	809	1186
12-14	.103	.018	2.0	1340	600	602	599
12-15	.118	0	3.0	1440	1014	1153	1274
12-16	.118	.018	2.1	1440	603	601	601
12-17	.103	.018	1.9	1340	603	602	601
12-18	.127	0	3.3	1500	1076	1282	1339
12-19	.127	.018	2.0	1500	605	603	603
12-20	.127	0	3.3	1500	1091	1297	1342
12-21	.118	0	2.9	1440	1049	1230	1269
12-22	.118	.010	2.0	1440	601	599	600
12-23	.118	.014	2.0	1440	601	599	600
12-24	.118	.018	1.8	1440	606	603	604
12-25	.118	.014	1.9	1440	609	606	607
12-26	.118	.010	1.8	1440	608	605	607
12-27	.118	0	2.8	1440	1061	1247	1288

$$P_o = 125 \pm 6 \text{ kPa}$$

$$T_o = 600 \pm 10 \text{ K}$$

$$\langle u_o \rangle = 14 \pm 5 \text{ m/s}$$

$$(X_{\text{H}_2\text{O}})_o = .005 \pm .0005$$

Average fuel composition (mole fractions):

$$\text{H}_2 \quad .412 \pm .013$$

$$\text{CO} \quad .194 \pm .001$$

$$\text{CH}_4 \quad .104 \pm .001$$

$$\text{CO}_2 \quad .290 \pm .011$$

Table 5-2 (Continued)

	T_s $z = 70$ mm (K)	T_s $z = 75$ mm (K)	$(T_g)_4$ $z = 77$ mm (K)	$\frac{(X_{H_2})_4}{(X_{H_2})_0}$	$\frac{(X_{CO})_4}{(X_{CO})_0 + (X_{CH_4})_0}$	$\frac{(X_{CH_4})_4}{(X_{CH_4})_0}$
12-13	1163	1106	1083	<.01	.12	.87
12-14	1173	1336	1288	.42	.59	.64
12-15	1269	1208	1163	<.01	.11	.71
12-16	906	1344	1346	.58	.62	.71
12-17	884	1268	1289	.68	.65	.83
12-18	1319	1259	1216	<.01	.13	.63
12-19	775	1311	1416	.61	.63	.76
12-20	1339	1282	1228	<.01	.11	.58
12-21	1209	1159	1133	<.01	.13	.81
12-22	1012	1363	1342	.35	.54	.60
12-23	1042	1379	1356	.39	.54	.64
12-24	913	1139	1380	.64	.63	.80
12-25	913	1140	1368	.62	.63	.73
12-26	927	1161	1366	.53	.60	.69
12-27	1233	1183	1141	<.01	.11	.79

Conversions of CH_4 with and without H_2S are indistinguishable within the precision of the data. Although Figures 5-11 and 5-15 appear to indicate that conversion of CH_4 is improved under some conditions by adding H_2S , the data are not sufficiently precise to establish this conclusion.

5c. Oxidation of Ammonia to Nitric Oxide

A series of experiments was performed in which NH_3 was introduced into the inlet stream during catalytic combustion of a medium-Btu gas. The purpose of this work was to determine the fraction of NH_3 impurity converted to NO in the reactor, and to examine the dependence, if any, of this conversion on equivalence ratio. The catalyst was a sample of Pt/ γ - Al_2O_3 /Cordierite in which a series of experiments with CO fuel, lasting 20-30 hours, had been performed. A flashback arrestor 13 mm long was placed 3 mm upstream of the catalyst. Because the sample had already been used under extreme conditions for a relatively long time when the medium-Btu/ NH_3 experiments were begun, it was necessary to use a high fuel/air preheat temperature (810 K) to achieve stable operation of the reactor. Under these conditions, a temperature rise was observed on the downstream side of the flashback arrestor and an unusually high temperature at the first thermocouple in the reactor ($z = 1$ mm from entrance) indicating that flashback to the arrestor had occurred.

This condition was observed consistently throughout the series of experiments. Its effect was to increase the effective length of the reactor, which, combined with the effects of the high preheat temperature and high substrate temperature used, resulted in very little (< 10 mole ppm) unburned hydrocarbon (CH_4) at the exit of the reactor, in contrast with the data presented in Sections 5a and 5b. It is possible that such "preignition", in systems in which the fuel concentration is above the lean flammability limit and the gas velocity sufficiently low, might be used to advantage. In any case, it must be taken into consideration in the design of combustors burning free hydrogen-containing fuels.

Runs were made at two adiabatic (substrate) temperatures. At each of these temperatures the dependence of NH_3 to NO conversion was examined as a function of NH_3 mole fraction and as a function of equivalence ratio. In order to vary equivalence ratio without changing the substrate temperature, it was necessary to vary the oxygen to nitrogen ratio of the oxidizer.

Therefore, in these experiments, the oxidizer was not air which was normally supplied by a compressor, but was a mixture of industrial grade nitrogen (99.995 mole %) and oxygen (99.6 mole %). In a series of experiments, then, the substrate temperature, inlet temperature, pressure, and volumetric flowrate (reference velocity) of reactants was fixed. The NH_3 flowrate was varied (over a range which had negligible effect on the other parameters) and the oxygen and nitrogen flowrates were varied with their total volumetric flowrate fixed. NO was measured with a chemiluminescent NO/ NO_x detector (Thermo-Electron Model 44). NO_2 was not measured because water was condensed from the sample in a salt-ice cooled trap, which changes the NO_2 concentration. The reported NO mole fractions are the measured values, not corrected to a reference condition.

It had been planned to run with equivalence ratios greater than 1. Several attempts to do this were made, but the catalyst was always extinguished as the equivalence ratio passed from lean to rich. A possible explanation is as follows. It has already been mentioned that the catalyst activity during these experiments was relatively low, although operation at $\phi < 1$ was quite stable. Now, to a first approximation, the temperature of the solid in a catalytic reactor seeks that value at which the rate of heat release by chemical reaction at the surface is equal to the rate at which heat diffuses into the gas stream. Suppose, for simplicity, that in the lean case the rate of heat release at the surface is determined by the rate at which fuel diffuses to the surface. Medium-Btu gases contain hydrogen, whose diffusion coefficient is relatively large, therefore substrate temperatures near the reactor entrance (before the H_2 is used up) tend to be high when burning these fuels. However, when the oxygen concentration is lower than stoichiometric, it is diffusion of O_2 to the surface which limits the rate of heat release there. Because the diffusion coefficient of O_2 is smaller than H_2 , the steady state substrate temperature drops to a lower value, which was evidently less than the ignition temperature in the present experiments.

The medium-Btu gas was supplied by MG Scientific Gases with the following composition (mole fractions):

H_2	.424
CO	.193
CH_4	.103
CO_2	.280

The NH_3 dopant was added to the N_2/O_2 flow in the test section through a separate injection grid upstream of the fuel injection grid. The flowrate of NH_3 was determined using a rotameter calibrated at the appropriate downstream pressure (110 kPa).

Experiments were done at the following conditions:

$$P_o = 110 \pm 5 \text{ kPa}$$

$$T_o = 810 \pm 20 \text{ K}$$

$$\langle u_o \rangle = 9 \pm 3 \text{ m/s}$$

$$X_{f,o} = .08 \quad (T_{ad} = 1384 \pm 14 \text{ K})$$

$$T_{s,max} \cong 1300 \text{ K}$$

$$= .11 \quad (T_{ad} = 1585 \pm 25 \text{ K})$$

$$T_{s,max} \cong 1470 \text{ K}$$

The oxidizer compositions, equivalence ratios, and mole fractions of NH_3 and NO are listed in Table 5-3. The highest mole fraction of CO observed at the catalyst exit at the lower adiabatic temperature was 1500 mole ppm. At the higher adiabatic temperature, CO was always less than 100 mole ppm. In some of the runs the thermocouple/sampling probe was moved downstream from the catalyst exit to observe changes in composition of the exhaust gas. X_{CO} decreased with distance, but X_{NO} remained constant within the precision of the measurement.

Figure 5-16 and 5-17 show the fractions of NH_3 converted to NO ($X_{\text{NO}}/X_{\text{N}}$) versus equivalence ratio for the two adiabatic temperatures. X_{N} represents the total mole fraction of all nitrogen-containing species formed from the NH_3 : $X_{\text{N}} = \sum_i X_{\text{N}_i}$ where N_i represents a class of nitrogen compounds formed from ammonia and containing i N atoms. Simply stated, X_{N} would be the mole fraction of NH_3 if no NH_3 decomposition occurred. X_{N} is not equal to $X_{\text{NH}_3,0}$ because of the change in average molecular weight of the gas in combustion. It is seen in Figures 5-16 and 5-17 that there is no significant dependence of NH_3 to NO conversion on equivalence ratio for the range and conditions studied. The only significant trend is the change in conversion with $X_{\text{NH}_3,0}$; that is, the greater the concentration of NH_3 , the smaller the fraction of it which is converted to NO. Although conversions greater than 1 were observed, they are not significantly greater. The average values of $X_{\text{NO}}/X_{\text{N}}$ and X_{NO} over all equivalence ratios for each $X_{\text{NH}_3,0}$ were computed, and these are shown in Figure 5-18. Conversion of NH_3 to NO is seen to be greater at the higher adiabatic temperature; and, although conversion decreases with $X_{\text{NH}_3,0}$, the absolute amount of NO at the catalyst exit increases as the inlet NH_3 increases. The error bars shown are the uncertainties in the calculated mean values (5-1/2 times error of Figures 5-16 and 5-17). The conversion of NH_3 to NO at $T_{\text{ad}} = 1585 \text{ K}$, $X_{\text{NH}_3,0} = .0006$ is greater than 1 by a barely significant amount. We doubt that this is due to anything but unexpected errors in the measurements. At each set of inlet conditions, a measurement of NO was made without addition of NH_3 . The readings were uniformly less than the sensitivity of the NO analyzer ($\sim 7 \text{ ppm}$).

Table 5-3. Species Mole Fractions and
Equivalence Ratios for Runs Using
Ammonia Doped Medium - Bt Gas

Run No.	X_{N_2/O_2}	X_{O_2/O_2}	ϕ	$X_{NH_3/f}$	$X_{NH_3,0}$ (mole ppm)	$X_{NO,4}$ (mole ppm)	$\frac{X_{NO,4}}{X_{N,4}}$	$\pm \epsilon$
13-199	.792	.208	.219	0	0	5	—	
200	.792	.208	.218	.007	581	584	.98	.34
201	.792	.208	.218	.016	1322	998	.73	.22
202	.793	.207	.218	.026	2113	1235	.57	.16
203	.792	.208	.218	.036	2999	1472	.48	.13
204	.817	.183	.248	.036	3010	1492	.48	.13
205	.817	.183	.248	.026	2129	1330	.61	.17
206	.816	.184	.250	.016	1331	1036	.76	.23
207	.817	.183	.250	.007	583	618	1.03	.36
208	.817	.183	.252	0	0	3	—	
209	.853	.147	.314	0	0	3	—	
210	.854	.146	.314	.007	580	608	1.02	.36
211	.853	.147	.314	.016	1324	978	.72	.22
212	.854	.146	.314	.025	2116	1273	.58	.16
213	.854	.146	.314	.035	2991	1539	.50	.14
214	.885	.115	.398	.035	2992	1606	.52	.14
215	.885	.115	.398	.025	2116	1354	.62	.17
216	.884	.116	.398	.016	1324	1045	.77	.23
217	.885	.115	.398	.007	580	627	1.05	.37
218	.884	.116	.398	0	0	3	—	
219	.915	.085	.542	0	0	3	—	
220	.915	.085	.542	.007	582	608	1.02	.36
221	.915	.085	.542	.016	1324	988	.73	.22
222	.915	.085	.542	.025	2125	1311	.60	.17
223	.915	.085	.542	.035	3005	1591	.52	.14
224	.912	.088	.725	.027	3006	2046	.65	.18
225	.912	.088	.725	.019	2126	1674	.76	.21

Table 5-3 (continued)

Run No.	$X_{N_2/OX}$	$X_{O_2/OX}$	ϕ	$X_{NH_3/f}$	$X_{NH_3,0}$ (mole ppm)	$X_{NO,4}$ (mole ppm)	$\frac{X_{NO,4}}{X_{N,4}}$	$\pm \epsilon$
13-226	.912	.088	.728	.012	1324	1232	.89	.27
227	.913	.087	.728	.005	580	730	1.21	.42
228	.912	.088	.732	0	0	6	—	
229	.881	.119	.537	0	0	4	—	
230	.881	.119	.537	.005	582	679	1.12	.39
231	.880	.120	.540	.012	1328	1246	.90	.27
232	.881	.119	.543	.019	2113	1660	.75	.21
233	.881	.119	.543	.026	2999	2092	.67	.18
234	.849	.151	.428	.026	2992	2083	.67	.18
235	.848	.152	.428	.019	2124	1693	.77	.22
236	.848	.152	.430	.012	1323	1256	.91	.27
237	.849	.151	.432	.005	579	684	1.14	.40
238	.849	.151	.432	0	0	4	—	
239	.816	.184	.357	0	0	4	—	
240	.815	.185	.359	.005	586	679	1.12	.39
241	.815	.185	.359	.012	1332	1251	.90	.27
242	.816	.184	.361	.018	2128	1655	.75	.21
243	.816	.184	.361	.026	3008	2060	.66	.18
244	.784	.216	.309	.026	3006	1981	.64	.17
245	.784	.216	.307	.018	2127	1628	.73	.20
246	.783	.217	.307	.011	1331	1246	.90	.27
247	.785	.215	.307	.005	581	744	1.23	.43
248	.783	.217	.307	0	0	4	—	

Nomenclature for Section 5

A	area, m^2 preexponential factor
C_k	concentration of species k, $kmol/m^3$
C_p	specific heat, $J/kg \cdot K$
D_k	diffusion coefficient of species k in air, m^2/s
E_a	activation energy, $J/kmol$
Le_k	Lewis Number = $\lambda / \rho D_k C_p$
$\dot{m}$	mass flowrate, kg/s
MBtu	medium-Btu
P	pressure, Pa
R_o	gas constant = $83.4 J/kmol \cdot K$
t	time, s
T	temperature, K
$\langle u \rangle$	average gas velocity, m/s , = $\dot{m} / \rho A$
$X_{j/k}$	mole fraction species j in k
Y_k	mass fraction species k
z	axial coordinate, m
ϵ	limit of error (1% confidence) $\cong 2.6\sigma$ for normal distribution
λ	thermal conductivity, $J/m \cdot s \cdot K$
ρ	density, kg/m^3
ϕ	equivalence ratio = $(Y_f/Y_{OX})(Y_f/Y_{OX})_{stoich}$

Subscripts

ad	adiabatic
f	fuel
g	gas
N	nitrogen-containing species derived from NH_3
OX	oxidizer
s	solid, surface, substrate
0,1,2,3,4	axial positions in test section, see Figure 3-4

6. Optical Measurement of Gas Temperature and Species Concentrations

6a. Proposed Systems for Making Optical Measurements in a Catalytic Reactor

The relatively small diameters of typical catalytic combustor monolith channels, and the importance of not disturbing the steady-state substrate temperature profile make it unlikely that reliable space-resolved measurements of gas temperatures and species concentrations can be obtained by introduction of probes into the reactor passages. Because such measurements would be of great value for the analysis of the relationship among the processes taking place, a study was made of unobtrusive techniques for performing these experiments.

The proposed catalyst arrangement for measurement of radical species concentrations in catalytic combustion by resonance absorption is shown in Fig. 6-1. Two pieces of catalytic monolith are mounted in the test section with a space between them. Using rectangular coordinates to describe the system: the flow is in the z direction, the exposed surfaces are parallel to the x - z plane, the y coordinate describes the vertical position relative to the surfaces, and the probing beam is parallel to the x axis. The composition of the gas in the space is a function only of z and y if conditions are sufficiently uniform in the x direction. The position of the laserbeam can be varied in z and y to determine the two-dimensional steady state distribution of species concentration. A schematic diagram of a system for making the measurements is shown in Fig. 6-2. The configuration of two parallel flat plates attached to intact monoliths was chosen to minimize radiative heat loss from the substrate to the surroundings. It is intended that the system be as nearly adiabatic as possible. However, the side openings of the configuration may have large effects on the substrate temperature, gas temperature, and gas composition, which must be evaluated.

The same catalyst arrangement might be used for making Raman scattering measurements, as shown in Fig. 6-3. The incident beam is now parallel to the flow (z direction), and radiation scattered in the x direction is collected. A system for measuring major species concentrations and gas temperature is shown in Fig. 6-4.

6b. A Pulsed, Multi-Pass Technique for Enhancement
of Raman Scattering*

In order to increase the photon yield without ensemble averaging over many laser pulses separated by times greater than the characteristic time scale of the combustion process it is proposed to use a multi-pass pulsed configuration. In this case the same laser pulse is successively passed through the scattering volume using an optical multi-pass cell. A number of optical multi-pass cell designs have been used for enhancement of CW Raman scattering (Hill and Hartley, 1974; Hill, et al., 1977); however, none of these designs are optimally suited for pulsed Raman scattering enhancement. The requirements of such a multi-pass cell are discussed below and a multi-pass design which maximizes the benefits of Pulsed Multi-pass Raman Scattering is presented.

*The work described in this section has been published by D. A. Santavicca, Optics Communications 30 (1979) 423.

Consider a laser pulse in a multi-pass cell where for a given initial laser pulse with n_0 photons, the actual number of photons, n_{tot} , which multi-pass through the scattering volume depends on the number of passes, N , and the losses ($= 1 - f$) in the multi-pass optics and in the scattering volume. This is represented by the following equation.

$$n_{tot} = \sum_{i=1}^N n_0 f^{(i-1)} \quad (6-3)$$

Fig. 6-5 shows the number of multi-pass photons normalized by the number of initial photons versus the number of passes for different transmission factors, f . These curves also represent the photon yield enhancement and as can be seen, above a certain number of passes, for a given transmission factor, there is no increase in the photon yield for increasing number of passes.

This leveling off of the photon yield enhancement also has an effect on the signal to noise ratio enhancement. The number of detected photons is given by

$$S_D = \eta(n_{stot} + n_{Btot}) \pm \sqrt{\eta(n_{stot} + n_{Btot})} \quad (6-4)$$

where both Raman scattered photons, n_{stot} , and background photons, n_{Btot} , are included and where Poisson statistics are used to describe the relative error. Similarly the number of independently detected background photons is given by

$$S_B = \eta n_{Btot} \pm \sqrt{\eta n_{Btot}} \quad (6-5)$$

The number of Raman scattered photons can be written as

$$n_{stot} = \sum_{i=1}^N n_{si} = \sum_{i=1}^N n_{so} f^{(i-1)} = n_{so} \sum_{i=1}^N f^{(i-1)} \quad (6-6)$$

where n_{si} is the number of Raman scattered photons per pass and n_{so} is the number of Raman scattered photons from the initial pass.

There are two types of background noise. For a constant level of background noise the number of photons is given by

$$n_{Btot} = \sum_{i=1}^N n_{Bi} = \sum_{i=1}^N n_{Bo} = n_{Bo} \sum_{i=1}^N 1 = n_{Bo} N \quad (6-7)$$

where n_{Bi} is the number of background photons incident on the detector during the time interval for one pass. For laser induced background noise the number of photons is given by

$$n_{Btot} = \sum_{i=1}^N n_{Bi} = \sum_{i=1}^N n_{Bo} f^{(i-1)} = n_{Bo} \sum_{i=1}^N f^{(i-1)} \quad (6-8)$$

where n_{Bo} is the number of laser induced background photons during the initial pass.

Substituting equations (6), (7), and (8) into equations (4) and (5), and then performing the background subtraction gives for the case of constant background noise.

$$S_D - S_B = \eta n_{so} \sum_{i=1}^N f^{(i-1)} \pm \sqrt{\eta(n_{so} \sum_{i=1}^N f^{(i-1)} + N n_{Bo})} \pm \sqrt{N \eta n_{Bo}} \quad (6-9)$$

and for the case of laser induced background noise

$$S_D - S_B = \eta n_{so} \sum_{i=1}^N f^{(i-1)} \pm \sqrt{\eta[n_{so} \sum_{i=1}^N f^{(i-1)} + n_{Bo} \sum_{i=1}^N f^{(i-1)}]} \pm \sqrt{\eta n_{Bo} \sum_{i=1}^N f^{(i-1)}} \quad (6-10)$$

In equations (9) and (10), taking the first term as the signal and the last two terms as the noise gives the following effective signal to noise ratios after background subtraction.

For the case of constant background noise

$$(S/N)^* = \frac{\sqrt{\eta n_{so} (n_{so}/n_{Bo})} \sum_{i=1}^N f^{(i-1)}}{\sqrt{N} + \sqrt{(n_{so}/n_{Bo}) \sum_{i=1}^N f^{(i-1)} + N}} \quad (6-11)$$

and for the case of laser induced background noise

$$(S/N)^* = \frac{\sqrt{\eta n_{so} (n_{so}/n_{Bo})} \sum_{i=1}^N f^{(i-1)}}{1 + \sqrt{1 + (n_{so}/n_{Bo}) \sum_{i=1}^N f^{(i-1)}}} \quad (6-12)$$

The effective signal to noise ratio after background subtraction for both types of background noise are plotted in Fig. 6-6 for typical quantum efficiency, η , number of single pass Raman scattered photons, n_{so} , and single pass signal to noise ratio, n_{so}/n_{Bo} . As Fig. 6-6 shows there is an optimum number of passes for achieving the maximum effective signal to noise ratio and the optimum number of passes depends on the transmission factor and on whether there is constant or laser induced background noise.

The inverse of the effective signal to noise ratio is equal to the accuracy of the measurement, therefore, solving equations 11 and 12 for ηn_{so} gives expressions for the minimum number of detected Raman photons required for a specified measurement accuracy with given number of detected background photons, transmission factor and number of passes. For constant background noise,

$$\eta n_{so} = \frac{n_{Bo} (S/N)^* \left[\frac{(S/N)^*}{n_{Bo}} + 2 \sqrt{\frac{\eta N}{n_{Bo}}} \right]}{\sum_{i=1}^N f^{(i-1)}} \quad (6-13)$$

and for laser induced background noise,

$$\eta n_{so} = \frac{n_{Bo} (S/N)^* \left[\frac{(S/N)^*}{n_{Bo}} + 2 \sqrt{\frac{\eta}{n_{Bo}} \sum_{i=1}^N f^{(i-1)}} \right]}{\sum_{i=1}^N f^{(i-1)}} \quad (6-14)$$

For a particular laser, optics, detector, combustion environment and molecular species one can calculate the number of detected Raman photons for different species densities. This was done for nitrogen and together with equations 13 and 14 used to plot the minimum detectability limit curves shown in Fig. 6-7 for the case of constant background noise and in Fig. 6-8 for the case of laser induced background noise. The different curves correspond to different measurement accuracies and different initial pass detected background noise levels. The constant background noise, ηn_{Bo} equal to 1 or 10 cases are typical of measurements in a very clean, noise-free flame where one is detector noise limited. For such cases when using a 100 to 200 pass, $f = 0.990$ pulsed multipass cell, measurements of nitrogen concentration as low as from 2×10^{16} to 5×10^{16} /cc with 10% accuracy and from 5×10^{16} to 10^{17} /cc with 5% accuracy are predicted. The laser induced background noise, ηn_{Bo} equal to 100, 500 or 1000 cases are typical of situations where laser induced fluorescence or particulate incandescence have been observed.* For these cases, using a 400 pass, $f = 0.990$ pulsed multipass cell, measurements of nitrogen concentrations as low as from 10^{17} to 3×10^{17} /cc with 10% accuracy are predicted. This last

*Eckbreth et al., 1977.

prediction is particularly interesting since the minimum detectability achieved to date using CARS in a sooting flame is $10^{17}/\text{cc CO}^*$. When using the results in Figs. 6-7 & 6-8 for species other than N_2 one must account for the differences in the vibrational Raman cross-section, the Stokes Q-branch bandwidth and the vibrational Raman wavenumber shift. The appropriate correction factors are given below for some diatomic molecules of interest. The predicted minimum detectable CO concentration using a pulsed multipass Raman cell is slightly less than that shown in Figs. 6-7 and 6-8.

MINIMUM DETECTABLE CONCENTRATION CORRECTION FACTORS

	$\Delta\omega_v$	$\sigma_v/\sigma_{v\text{N}_2}$	$\Delta\lambda^+$	$X_{\text{MIN}}/X_{\text{N}_2\text{MIN}}$
N_2	2311 cm^{-1}	1.0	15 $\text{\AA}$	1.0
CO	2143	1.2	15	0.72
NO	1877	0.55	15	1.63
H_2	4155	2.2	40	1.94
O_2	1556	1.2	15	0.69

⁺the entire Stokes vibrational Q-branch spectra bandpass
for T = 2000 K

There are three potential limitations in the application of Pulsed Multipass Raman scattering to a particulate laden environment. One is related to the assumption that the incandescence decay time, which is related to the particulate size distribution, is less than the multipass time. If this is not the case then the constant background noise, η_{BO} equal to 500 case is more representative of laser induced particulate incandescence and for this case using a 130 pass, $f = 0.990$ pulsed multipass cell, measurements of nitrogen, as low as $4 \times 10^{17}/\text{cc}$ with 10% accuracy are predicted. The other two potential problems occur when there is appreciable particulate absorption causing significant attenuation of the multipass beam and if the total multipass time is comparable to the relevant heat transfer times causing perturbation of the local gas temperature. Those two effects depend on the actual particulate size distribution and number density.

*Eckbreth et al., 1978.

Several features of the Pulsed Multipass Raman cell are apparent from the preceding discussion.

- i. the single pass transmission factor, f , should be as large as possible, preferably .99 or greater.
- ii. the optimum number of passes can vary typically between 100 and 600 depending on the measurement conditions.
- iii. the time between passes should be comparable to the single pulse width.
- iv. the initial single pulse peak power should approach the gas breakdown limit.

Fig. 6-9 shows a schematic drawing of a pulsed multipass cell design which satisfies these requirements. The basic feature of this multipass cell design is that of admitting 1.06μ radiation into a multipass cell cavity where it is partially converted to 532 nm with a Brewster angle mounted second harmonic generating (SHG) crystal. The 532 nm radiation is trapped in the mirrored cavity while the remaining 1.06μ radiation is dumped. This design is capable of the desired 0.99 single pass transmission factor by using state of the art dielectric coatings and Brewster's angle mounted optics. Note that the transmission losses are not symmetric about the probe volume. The number of passes is selected by using gated detection electronics such as a boxcar integrator. The cavity mirrors, if made highly reflective at 532 nm, only transmit between 85% to 95% of the 1.06μ radiation which results in substantial amounts of 1.06μ radiation being reflected back into the laser cavity and possibly causing permanent damage to the oscillator rod. Therefore it is essential to isolate the laser from the retro-reflected 1.06μ radiation.

Isolation can be achieved using a Faraday rotator isolator and if a type I KD*P SHG crystal is used, so as not to change the polarization of the 1.06μ radiation, then the residual 1.06μ after the SHG can be reflected back through the SHG for additional 532 nm generation.

In the absence of a Faraday rotator isolator the pulsed multipass cell concept as proposed herein has been demonstrated with the multipass cell configuration shown in Fig. 6-10. Brewster's angle, 90° deviation dispersion prisms are used for separating the 1.06μ and trapping the 532 nm radiation. This configuration is less efficient than the configuration shown in Fig. 6-9 due to the greater number of surfaces in the multipass cavity; however, it does serve to demonstrate the potential of this technique. The multipass cell performance is monitored by detecting the Rayleigh scattered light at a point in the multipass beam. Typical performance achieved with this multipass cell is shown in figure 25. The 532 nm multipass cavity length is 20 feet resulting in an approximate 40 nsec cavity round trip time. Fig. 6-11 shows that the signal decreases to 10% of its initial strength in 800 nsec or 40 passes. This corresponds to an average single pass transmission efficiency of 94.4%, and results in a signal enhancement of 17 over that for the single pass case. In other words this is equivalent to having an 800 nsec long laser pulse which has 17 times the energy of the single pass pulse. To date the largest single pass pulse energy which has been used is 40 mJ corresponding to a 680 mJ multipass pulse. The laser which has been used in this work is a Quanta-Ray Nd:YAG Model DCR-1A which delivers up to 700 mJ/pulse at 1.06μ . Using the multipass configuration shown in Fig. 6-9 it is reasonable to expect 98% transmission efficiencies resulting in 1 μ sec long laser pulses with 50 times the energy of the single pass pulse. With 700 mJ/pulse at 1.06μ available multipass pulse energies of 10 Joules are expected.

A complete system for applying the pulsed multipass Raman scattering technique for species concentration measurements in catalytic combustion is shown in Fig. 6-12. The catalyst arrangement is the same as that suggested for single pass Raman scattering measurements, Fig. 6-3.

NOMENCLATURE FOR SECTION 6

N	= number of passes
n_o	= number of incident photons in initial laser pulse
n_{tot}	= total number of multipass photons
n_{stot}	= total number of multipass Raman scattered photons to reach the detector
n_{Btot}	= total number of background photons to reach the detector during the multipass interval
n_{si}	= number of Raman scattered photons to reach the detector per pass
n_{so}	= number of Raman scattered photons to reach the detector from initial pass
n_{Bi}	= number of background photons incident on the detector during the time interval for one pass
n_{Bo}	= number of background photons incident on the detector during the initial pass
p_k	= partial pressure of species k, Pa
p	= pressure, Pa
B_o	= gas constant = 8314 J/K-kmol
S_B	= total number of detected background photons
S_D	= total number of detected Raman photons
$(S/N)^*$	= effective signal to noise ratio for multipass system after background subtraction
t	= time, s
T	= temperature, K
η	= detector quantum efficiency
ρ	= density, kg/m ³

7. Conclusions

The strategy of decoupling parts of complex problems through the use of experimentally measured properties of the system has been fruitfully applied to the analysis of reactive flow in a non-isothermal tubular reactor with catalytic wall. In the present case the approach was to use experimentally determined wall temperatures and to concentrate on solving the gas phase equations.

This combination of experimental and theoretical work has been applied to combustion of CO in a Pt/ γ -Al₂O₃/Cordierite monolith. In addition to the measured wall temperature, inclusion of gas and wall chemical reactions, with axial and radial convection and diffusion of species, heat, and momentum was sufficient to accurately reproduce the observed variation of unburned CO and pressure drop with gas velocity. For the catalyst and regime investigated it was found that a satisfactory description of the system could not be obtained without modeling both gas and wall reactions.

The experimental study of combustion of a medium-Btu gas in the Pt/ γ -Al₂O₃/Cordierite catalyst established some characteristics of this system. H₂ was by far the easiest fuel component to oxidize and was only seen in very small amounts in the reactor exhaust. CH₄ required the highest temperature for significant conversion, but once oxidation started it disappeared rapidly. CO underwent some oxidation even at the lowest temperatures, but its oxidation rate increased only slowly with temperature. This was probably because homogeneous CO oxidation was slow in the presence of CH₄ so that CO only reacted at the wall. The rate of wall reaction cannot be faster than the rate that reactants arrive there, and diffusion rates only increase approximately as $T^{1.5}$.

When H₂S was added to the medium-Btu gas, the substrate temperature dropped in the front half of the monolith. The maximum substrate temperature remained approximately the same, only shifted downstream. The catalyst was not extinguished, although its operation may have depended on its acting as a flameholder (fuel/air mixture may have been above lean flammability limit) with heating of the substrate by the flame. When the H₂S flow was stopped, the catalyst always returned to approximately the same condition as had existed before the H₂S was added. This indicated that the effects of H₂S on the operation of the catalyst were reversible.

Conversion of NH₃ to NO was independent of equivalence ratio in the range investigated. Conversion depended, however, on the amount of NH₃ present, being complete at low concentrations and decreasing with increasing mole fraction of NH₃. Conversion of NH₃ to NO increased with increasing substrate temperature for all equivalence ratios and NH₃ mole fractions. When no NH₃ was present NO was below the detectability limit of the analyzer (7 mole ppm).

For all fuels studied it was noted that substrate temperature is roughly proportional to adiabatic temperature but insensitive to change in gas velocity.

Observation of the rates of CO disappearance in the catalytic reactor exhaust during CO, medium-Btu gas, and C_3H_8 combustion were consistent with known homogeneous rates and mechanisms, therefore the exhaust can probably be treated simply as a reacting gas not influenced by the particular nature of the catalytic section upstream.

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Figure 3-1. Flow reactor for the study of catalytic combustion.

Figure 3-2. Arrangement of the fuel injection grid.

Tube diameter, outside 1.6 mm
inside 1.1 mm

Hole diameter 0.34 mm

Figure 3-3. Substrate temperature vs. radial position, C_3H_8 combustion. (axial position = 50 mm from catalyst inlet)

- a 0.217 ± 0.001 m
- b 0.0132 OR 0.0262 ± 0.0003 OR 0
- c 0.001 TO 0.003
- d 0.0760 ± 0.0003
- e 0.0010 ± 0.0005

Figure 3-4. Arrangement of catalyst, flashback arrestor, and probes.

Figure 3-5. Oxidizer, fuel, fuel dopant, and sample flows.

substrate	gas	ϕ	$T_{ad}(K)$
●	O	$0.24 \pm 0.03 = \phi_1$	1470 ± 80
▲	Δ	$1.10 \phi_1$	1540 ± 80
▼	∇	$1.22 \phi_1$	1610 ± 80

Figure 4-1. Substrate temperature and exhaust temperature vs. axial position at different equivalence ratios, CO combustion.

$$P_O = 112 \pm 4 \text{ kPa}$$

$$T_O = 700 \pm 10 \text{ K}$$

$$u_O = 19 \pm 5 \text{ m/s}$$

Figure 4-2. Exhaust composition vs. axial position at different equivalence ratios, CO combustion. Same conditions as Figure 4-1.

Figure 4-3. Substrate temperature and exhaust temperature vs. axial position, CO combustion.

$$P_o = 109 \pm 4 \text{ kPa}$$

$$T_o = 700 \pm 10 \text{ K}$$

$$\phi = 0.24 \pm 0.02$$

$$u_o = 15 \pm 5 \text{ m/s}$$

Figure 4-4. Substrate temperature and exhaust temperature vs. axial position, CO combustion.

$$u_o = 21 \pm 5 \text{ m/s}$$

P_o, T_o, ϕ same as Figure 4-3.

Figure 4-5. Substrate temperature and exhaust temperature vs. axial position, CO combustion.

$$u_o = 30 \pm 5 \text{ m/s}$$

P_o , T_o , ϕ same as Figure 4-3.

∇ $\circ$ Δ Measured mole fractions
 $\blacktriangledown$ $\bullet$ $\blacktriangle$ Theoretical predictions
 $A_s = 3.82 \times 10^3 \text{ m/s}$
 no chemisorption term

u_o (m/s)
 ∇ 15 ± 5
 $\circ$ 21 ± 5
 Δ 30 ± 5

Figure 4-6. Exhaust composition vs. axial position
 at different reference velocities, CO combustion.
 P_o , T_o , ϕ same as Figure 4-3.

- Experimental points
- △ Theoretical predictions, finite surface reaction rate,
 $A_s = 3.82 \times 10^3 \text{ m/s}$
 no chemisorption term

Figure 4-7. Observed and predicted ratios of unburned CO to inlet CO vs. reference velocity, CO combustion.

$$P_o = 109 \pm 4 \text{ kPa}$$

$$T_o = 700 \pm 10 \text{ K}$$

$$\phi = .19 - .30$$

$$X_{H_2O} = .011 - .037$$

$$\text{Maximum Substrate Temperature} = 1340 \pm 90 \text{ K}$$

Figure 4-8. Pressure drops observed and predicted vs. reference velocity, CO combustion.

$P_0 = 109 - 112$ kPa

$T_0 = 700$ K

$\phi = 0.23 - 0.24$

$A_s = 3.82 \times 10^3$ m/s, no chemisorption term

Figure 4-9. Arrhenius plot of rate coefficients for CO oxidation in the exhaust, CO combustion. Solid line: Howard, Williams, and Fine (1973).

Figure 4-10. Calculated fuel mass fractions and gas temperatures versus radial position, CO combustion.

$$P_o = 109 \text{ kPa}$$

$$T_o = 700 \text{ K}$$

$$\phi = 0.24$$

$$u_o = 30 \text{ m/s}$$

$$Re = 1036$$

$$A_s = 3.82 \times 10^3 \text{ m/s, no chemisorption term}$$

Figure 4-11. Calculated fuel mass fractions and gas temperatures versus axial position, CO combustion.

$$P_o = 109 \text{ kPa}$$

$$T_o = 700 \text{ K}$$

$$\phi = 0.24$$

$$u_o = 30 \text{ m/s}$$

$$Re = 1036$$

$$A_s = 3.82 \times 10^3 \text{ m/s, no chemisorption term}$$

Figure 4-12. Calculated fuel mass fractions and gas temperatures versus radial position, CO combustion.

$$P_0 = 112 \text{ kPa}$$

$$T_0 = 700 \text{ K}$$

$$\phi = 0.19$$

$$u_0 = 5 \text{ m/s}$$

$$Re = 176$$

$$A_s = 3.82 \times 10^3 \text{ m/s, no chemisorption term}$$

Figure 4-13. Calculated fuel mass fractions and gas temperatures versus axial position, CO combustion.

$$P_0 = 112 \text{ kPa}$$

$$T_0 = 700 \text{ K}$$

$$\phi = 0.19$$

$$u_0 = 5 \text{ m/s}$$

$$Re = 176$$

$$A_s = 3.82 \times 10^3 \text{ m/s, no chemisorption term}$$

Figure 5-1. Substrate and gas temperatures versus axial position at different reference velocities, medium-Btu gas combustion.

$P_o = 120$ kPa

$T_o = 400$ K

$(X_{fuel})_o = 0.122$

$T_{ad} = 1280$ K

● ▲ ▼ substrate temperature

○ △ ▽ gas temperature

△ ▲ first run of series (Run #12-1)

▽ ▼ last run of series (Run #12-5)

Figure 5-2. Unburned fuel species versus axial position, medium-Btu gas combustion.

$$P_o = 120 \text{ kPa}$$

$$T_o = 400 \text{ K}$$

$$(X_{\text{fuel}})_o = 0.122$$

$$\langle u_o \rangle = 19.4 \text{ m/s}$$

Figure 5-3. Unburned fuel species at the catalyst exit versus reference velocity, medium-Btu gas combustion.

$P_o = 120 \text{ kPa}$

$T_o = 400 \text{ K}$

$(\dot{X}_{\text{fuel}})_o = 0.122$

$T_{\text{ad}} = 1280 \text{ K}$

Figure 5-4. Unburned fuel species versus axial position, medium-Btu gas combustion.

$P_0 = 120 \text{ kPa}$

$T_0 = 400 \text{ K}$

$(X_{\text{fuel}})_0 = 0.154$

$\langle u_0 \rangle = 5.0 \text{ m/s}$

Figure 5-5. Unburned fuel species versus axial position, medium-Btu gas combustion.

$$P_o = 120 \text{ kPa}$$

$$T_o = 590 \pm 11 \text{ K}$$

$$(X_{\text{fuel}})_o = 0.122$$

$$\langle u_o \rangle = 7.1 \text{ m/s}$$

Figure 5-6. Unburned fuel species at the catalyst exit versus adiabatic temperature, medium-Btu gas combustion.

$P_0 = 120 \text{ kPa}$

$T_0 = 400, 590 \text{ K}$

$(X_{\text{fuel}})_0 = .059 - .154$

$\langle u_0 \rangle = 4.5 - 7.1 \text{ m/s}$

$$\frac{dC_{CO}}{dt} = - C_{CO} C_{O_2}^{\frac{1}{4}} C_{H_2O}^{\frac{1}{2}} A \exp(-E_a/R_0 T)$$

Figure 5-7. Arrhenius plot of rate coefficients for CO oxidation in the exhaust from catalytic combustion of CO, medium-Btu gas, and C_3H_8 .

- CO
- ▽ Medium-Btu gas
- △ C_3H_8

- a. Dryer and Glassman, 1973, CO from CH_4 oxidation.
- b. Dryer and Glassman, 1973, moist CO oxidation.
- c. Kozlov, 1959, moist CO oxidation

Figure 5-8. Substrate temperature versus mole fraction of H_2S in fuel, medium-Btu gas combustion.

$$P_o = 125 \pm 6 \text{ kPa}$$

$$T_o = 600 \pm 5 \text{ K}$$

$$(X_f)_o = 0.118$$

$$\langle u_o \rangle = 14 \pm 1 \text{ m/s}$$

Figure 5-9. Fraction of H_2 unconverted versus mole fraction of H_2S in fuel, medium-Btu gas combustion.

$$P_o = 125 \pm 6 \text{ kPa}$$

$$T_o = 600 \pm 5 \text{ K}$$

$$(X_f)_o = 0.118$$

$$\langle u_o \rangle = 14 \pm 1 \text{ m/s}$$

Figure 5-10. Fraction of CO unconverted versus mole fraction of H₂S in fuel, medium-Btu gas combustion.

$$P_0 = 125 \pm 6 \text{ kPa}$$

$$T_0 = 600 \pm 5 \text{ K}$$

$$(X_f)_0 = 0.118$$

$$\langle u_0 \rangle = 14 \pm 1 \text{ m/s}$$

Figure 5-11. Fraction of CH_4 unconverted versus mole fraction of H_2S in fuel, medium-Btu gas combustion.

$$P_o = 125 \pm 6 \text{ kPa}$$

$$T_o = 600 \pm 5 \text{ K}$$

$$(X_f)_o = 0.118$$

$$\langle u_o \rangle = 14 \pm 1 \text{ m/s}$$

○ NO H_2S

△ $X_{H_2S}=0.018$ IN FUEL

Figure 5-12. Maximum substrate temperature versus adiabatic temperature, with and without H_2S , medium-Btu gas combustion.

$$P_0 = 125 \pm 6 \text{ kPa}$$

$$T_0 = 600 \pm 5 \text{ K}$$

$$(X_f)_0 = 0.103, 0.118, 0.127$$

$$\langle u_0 \rangle = 14 \pm 1 \text{ m/s}$$

○ NO H₂S
 △ X_{H₂S}=0.018 IN FUEL

Figure 5-13. Fraction of H₂ unconverted versus adiabatic temperature, with and without H₂S, medium-Btu gas combustion.

P₀ = 125 ± 6 kPa

T₀ = 600 ± 5 K

(X_f) = 0.103, 0.118, 0.127

<u₀> = 14 ± 1 m/s

○ NO H₂S

△ X_{H₂S} = 0.018 IN FUEL

Figure 5-14. Fraction of CO unconverted versus adiabatic temperature, with and without H₂S, medium-Btu gas combustion.

P₀ = 125 ± 6 kPa

T₀ = 600 ± 5 K

(X_f)₀ = 0.103, 0.118, 0.127

<u₀> = 14 ± 1 m/s

○ NO H₂S

△ X_{H₂S} = 0.018 IN FUEL

Figure 5-15. Fraction of CH₄ unconverted versus adiabatic temperature, with and without H₂S, medium-Btu gas combustion.

$$P_0 = 125 \pm 6 \text{ kPa}$$

$$T_0 = 600 \pm 5 \text{ K}$$

$$(X_f)_0 = 0.103, 0.118, 0.127$$

$$\langle u_0 \rangle = 14 \pm 1 \text{ m/s}$$

Figure 5-16. Fraction of NH_3 converted to NO_2 versus equivalence ratio, medium-Btu gas combustion.

$$T_{ad} = 1585 \pm 25 \text{ K}$$

Figure 5-17. Fraction of NH_3 converted to NO versus equivalence ratio, medium-Btu gas combustion.

Figure 5-18. Fraction of NH_3 converted to NO, and mole fraction of NO versus mole fraction of NH_3 at inlet, medium-Btu gas combustion.

Figure 6-1. Catalyst configuration and beam path for resonance absorption measurements.

Figure 6-2. Resonance absorption system for measuring species concentrations.

1. Quanta-Ray Nd:YAG Laser Model DCR-1A.
2. Quanta-Ray Harmonic Generator Model HG-1.
3. Quanta-Ray Tunable Pulsed Dye Laser Model PDL-1 with SHG and Mixing Crystals.
4. Beam splitter.
5. Lens.
6. Test section (seen from the end).
7. Filter.
8. RCA Photomultiplier Tube Model C31034.
9. PPI Amplifier Model 2A32.
10. High voltage power supply.
11. Evans Assoc. gated integrator.
12. Tektronix Storage Oscilloscope Model 7623A.
13. Hewlett Packard 21MX minicomputer.

Figure 6-3. Catalyst configuration and incident and scattered beam paths for Raman scattering measurements.

Figure 6-4. Pulsed Raman scattering system for measuring species concentrations and gas temperature.

1. Quanta-Ray Nd:YAG Laser Model DCR-1A.
2. Quanta-Ray Harmonic Generator Model HG-1.
3. Beam splitter.
4. Lens.
5. Test section (seen from the top).
6. Catalyst.
7. Collection Optics.
8. RCA Photomultiplier Tube Model C31034.
9. High voltage power supply.
10. PPI Amplifier Model 2A32.
11. Evans Assoc. gated integrator.
12. Tektronix Storage Oscilloscope Model 7623A.
13. PAR Boxcar Averager Model 162/164.
14. Hewlett Packard 21MX minicomputer.

Figure 6-5. Normalized number of multipass photons versus number of passes.

Figure 6-6. Enhancement of the effective signal to noise ratio after background subtraction.

Figure 6-7. Minimum detectable nitrogen concentration versus number of passes with constant background noise, Stokes vibrational Q-branch band pass of 15 Å, 200 mJ, 8 nsec, 532 nm initial laser pulse, 1 mm scattering volume length, 0.1 str collection angle, 0.54 collection optics transmission factor, 0.15 detector quantum efficiency and 0.990 multipass optics transmission factor.

Figure 6-8. Minimum detectable nitrogen concentration versus number of passes with laser-induced background, Stokes vibrational Q-branch bandpass of 15 Å, 200 mJ, 8 nsec, 532 nm initial laser pulse, 1 mm scattering volume length, 0.1 str collection angle, 0.54 collection optics transmission factor, 0.15 detector quantum efficiency and 0.990 multipass optics transmission factor.

Figure 6-9. Pulsed multipass cell.

Figure 6-10. Pulsed multipass cell experiment.

Figure 6-11. Comparison of Rayleigh scattering signal for single pass and multipass cases.

1. Quanta-Ray Nd:YAG Laser, Model DCR-1A
2. Quanta-Ray Faraday Rotator Isolator, Model FRI-1
3. Mirror
4. Brewster's Angle Cut, Type I KD*P, SHG Crystal
5. Lens
6. Catalyst
7. Collection Optics
8. RCA Photomultiplier Tube, Model C31034
9. High Voltage Power Supply
10. PPI Amplifier, Model 2A32
11. Evans Assoc. Gated Integrator
12. Tektronix Storage Oscilloscope, Model 7623A
13. PAR Boxcar Averager, Model 162/164
14. Hewlett Packard 21MX Minicomputer

Figure 6-12. Pulsed multipass Raman scattering experiment.

APPENDIX A: Radial Profiles of Gas Properties Upstream of the Catalytic Reactor*

Carbon Monoxide Experiments

Figure A-1 shows temperature profiles obtained by traversing the width of the test section with the pitot/thermocouple probe. These measurements were made with CO being injected and combustion taking place. The uniformity is independent of air flowrate over the range of velocities used. Sufficient fuel/air mixing was obtained only by placing baffles downstream of the fuel injector, and these affected the velocity profile. By trying various configurations, the velocity uniformity was improved while maintaining an even distribution of fuel. The arrangement used during the experiments consisted of two screens, each containing four 8 mm diameter holes, placed 30 and 110 mm downstream of the fuel injector. Another screen perforated with 1.6 mm diameter holes was 190 mm from the injector and 50 mm upstream of the pitot tube. The resulting fuel distribution is shown in Figure A-2. There is good uniformity over the measured range, however the largest equivalence ratio shown is a factor of 2 to 5 lower than those at which the reactor was run. This is due to the limited range of the CO analyzer (maximum CO - 3 mol%). Velocity profiles, shown in Figure A-3 are less satisfactory (range $\pm 10\%$). These were later improved by replacing the second screen by one containing five 6 mm diameter holes, which gave a velocity range of $\pm 6\%$. Average reference velocities were determined using the CO and air flowrates, inlet temperature and pressure, and the cross-sectional area of the catalyst.

Propane Experiments

The propane was injected through a grid of 25 holes. The air flowrate and equivalence ratio were used to compute the average reference velocity. Equivalence ratio was found by analysis of samples from the inlet stream. Baffles were used to promote mixing of the fuel and air. Typical radial profiles measured using the pitot/static/thermocouple/sampling probe are shown in Figures A-4 to A-6. Gas temperature and equivalence ratio were uniform within $\pm 1\%$ in a region covering 80% of the width of the duct, and velocity was uniform within $\pm 6\%$ over 50% of the width.

Medium-Btu Gas Experiments

A new fuel injection grid, shown in Figure 3-2, was installed for the medium-Btu gas experiments. It consisted of five tubes, each containing four holes. The air flowrate was measured to determine average inlet velocity, and equivalence ratio was found by analysis of samples from the inlet stream. The pitot tube and thermocouple probe was used to

* Radial profile data were collected with the assistance of B. Kim.

measure inlet velocity and temperature and also to extract samples. The probe traversed the inlet stream for measurement of the radial profiles of the temperature, velocity, and fuel concentration.

Radial temperature gradients were minimized by insulating the test section. The profiles measured during the Medium-Btu Gas experiments are shown in Figures A-7 and A-8. The deviation of the temperature is less than $\pm 1\%$ of the absolute temperature, over a region covering 80% of the width of the duct. The velocity profiles were improved by removing the baffles which had been introduced to promote mixing of the fuel and air. The measured profiles are shown in Figures A-9 and A-10. The deviation in the region covering 80% of the width of the duct varies from $\pm 17\%$ at the lowest velocity to $\pm 7\%$ at the highest velocity, which is the desired trend. The radial distribution of the medium-Btu gas was determined by analyzing the samples taken from the inlet stream for CO_2 , which is a constituent (30 mole %) of the fuel. The measured profiles are shown in Figures A-11 and A-12. The largest deviation observed is $\pm 3\%$ of the average CO_2 mole fraction.

NOMENCLATURE FOR APPENDIX A

P	pressure, Pa
T	temperature, K
u	velocity, m/s
x_k	mole fraction component k
ϕ	equivalence ratio
$\langle \rangle$	average

Subscripts

o	reference
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APPENDIX A FIGURES

- A-1. Inlet gas temperature vs. radial position - CO.
- A-2. Inlet fuel concentration vs. radial position - CO.
- A-3. Inlet gas velocity vs radial position - CO.
- A-4. Radial profiles of temperature upstream of the catalyst - C_3H_8 .
- A-5. Radial profiles of fuel mole fraction upstream of the catalyst - C_3H_8 .
- A-6. Radial profiles of gas velocity upstream of the catalyst - C_3H_8 .
- A-7. Reference temperature vs. radial position at different reference velocities - medium-Btu gas.
- A-8. Reference temperature vs. radial position at different fuel/air ratios - medium Btu gas.
- A-9. Reference velocity vs. radial position at different reference velocities - medium-Btu gas.
- A-10. Reference velocity vs. radial position at different fuel/air ratios - medium-Btu gas.
- A-11. Reference mole fraction CO_2 vs. radial position at different reference velocities - medium-Btu gas.
- A-12. Reference mole fraction CO_2 vs. radial position at different fuel/air ratios - medium-Btu gas.

Figure A-1. Inlet gas temperature vs. radial position - CO .
 $P_0 = 112 \text{ kPa}$

Figure A-2. Inlet fuel concentration vs. radial position - CO .

P = 112 kPa

T = 700 K

u = 60 m/s

Figure A-3. Inlet gas velocity vs. radial position - CO ..

$P_o = 112$ kPa

$T_o = 700$ K

Figure A-4. Radial profiles of temperature upstream of the catalyst - C_3H_8 .

$$P_0 = 110 \text{ kPa}$$

$$\phi = 0.28 \pm 0.01$$

$$u_0 = 9 \text{ m/s}$$

Figure A-5. Radial profiles of fuel concentration upstream of the catalyst - C_3H_8 .

$P_o = 110$ kPa

$T_o = 750$ K

$u_o = 6$ m/s

Figure A-6. Radial profiles of gas velocity upstream of the catalyst - C_3H_8 .

$P_0 = 110 \text{ kPa}$

$T_0 = 750 \text{ K}$

Figure A-7. Reference temperature versus radial position at different reference velocities - m Btu gas.

$$P_o = 120 \text{ kPa}$$

$$(X_{\text{fuel}})_o = 0.122$$

Figure A-8. Reference temperature versus radial position at different fuel/air ratios- M Btu gas.

$P_0 = 120 \text{ kPa}$

$\langle u_0 \rangle = 4.5 - 5.0 \text{ m/s}$

Figure A-9. Reference velocity versus radial position at different reference velocities - M-Btu gas.

$P_o = 120 \text{ kPa}$

$T_o = 400 \text{ K}$

$(X_{\text{fuel}})_o = 0.122$

Figure A-10. Reference velocity versus radial position at different fuel/air ratios - M Btu gas.

$P_0 = 120 \text{ kPa}$

$T_0 = 400 \text{ K}$

$\langle u_0 \rangle = 4.5 - 5.0 \text{ m/s}$

Figure A-11. Reference mole fraction CO₂ versus radial position at different reference velocities - M Btu gas.

$$P_o = 120 \text{ kPa}$$

$$T_o = 400 \text{ K}$$

$$(x_{\text{fuel}})_o = 0.122 \quad ((x_{\text{CO}_2})_o = 0.3(x_{\text{fuel}})_o)$$

Figure A-12. Reference mole fraction CO_2 versus radial position at different fuel/air ratios - M Btu gas.

$$P_o = 120 \text{ kPa}$$

$$T_o = 400 \text{ K}$$

$$(x_{CO_2})_o = 0.3(x_{fuel})_o$$

$$\langle u_o \rangle = 4.5 - 5.0 \text{ m/s}$$

APPENDIX B: Experimental Results on Propane/Air*

Propane/air combustion in the Pt/ γ -Al₂O₃/Cordierite catalyst was investigated for the following inlet conditions:

Inlet temperature (T_0) = 650 - 800 K

Inlet pressure (P_0) = 110 kPa

Reference velocity $\langle u_0 \rangle$ = 6 - 24 m/s

Equivalence ratio (ϕ) = 0.19 - 0.32

The catalyst sample was pretreated by burning propane for two hours with the maximum substrate temperature at 1480 K. Reference velocity, equivalence ratio, and inlet temperature were each varied separately with the other parameters fixed; the conditions for each run are listed in Table B-1. The average gas velocity just after entering the catalyst, taking into the account the fraction of open monolith area, is $1.67 \pm .06$ times the average reference velocity. CO, CO₂, HC, and O₂ concentrations were measured as functions of axial position in the exhaust. Pressure was also measured inside the catalyst by introduction of taps at 3 locations.

Figure B-1 shows substrate temperature, exhaust temperature, and HC and CO emissions at different equivalence ratios. At the lowest equivalence ratio (0.19), the gas temperature rise from inlet to outlet is only 200 K. About $\frac{1}{2}$ of the hydrocarbon is consumed, CO is less than 0.01 mol%, and very little additional reaction occurs downstream of the catalyst. When the equivalence ratio is increased to 0.22, a larger fraction of the hydrocarbon is burned, and some reaction can be observed in the exhaust as a decrease in HC and an increase in CO. With further increase in equivalence ratio (0.25), hydrocarbon disappears rapidly, and CO passes through a maximum. At the highest equivalence ratio (0.28), the amount of hydrocarbon at the catalyst exit is only 0.01 mol%, and the position of maximum integrated CO concentration is inside the catalyst.

Data obtained at different inlet gas temperatures are shown in Figure B-2. The main features and trends in the temperature and species profiles are analogous to those observed when equivalence ratio is varied.

The effects of changing gas velocity are shown in Figures B-3 and B-4. Substrate temperature is less sensitive to variation of velocity than to variation of equivalence ratio or inlet temperature. However, some changes in the shape of the substrate temperature profile can be seen; they need to be investigated further.

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Table B-1. Experimental test conditions, C_3H_8 /air combustion.
Pt/ γ - Al_2O_3 /Cordierite catalyst, 24 x 24 x 76 mm

Run No.	P_o (kPa)	T_o (K)	ϕ	u_o (m/s)	$(H_2O)_o$ (mol%)	$\Delta P/P_o$ (%)	T_{ad} (K)
11-2	110	750	.30	6	1.3	1.2	1480
11-3	110	750	.29	12	1.2	2.5	1460
11-4	110	750	.32	24	1.4	5.6	1520
11-5	110	750	.19	9	1.5	1.3	1230
11-6	110	750	.22	9	1.6	1.4	1300
11-7	110	750	.25	9	1.7	1.6	1370
11-8	110	750	.28	9	1.6	1.8	1430
11-9	110	650	.28	9	1.2	1.9	1350
11-10	110	700	.28	9	1.2	1.9	1390
11-11	110	800	.27	9	1.3	1.8	1450

NOMENCLATURE FOR APPENDIX B

HC hydrocarbon (reported as C_3)

P pressure, Pa

T temperature, K

u gas velocity, m/s

ϕ equivalence ratio

< > average

Subscripts

ad adiabatic (reaction temperature)

o reference condition

1 axial position just inside the catalyst entrance

APPENDIX B FIGURES

- B-1. Axial profiles of temperature and species at different equivalence ratios, C_3H_8 combustion.
- B-2. Axial profiles of temperature and species at different inlet temperature, C_3H_8 combustion.
- B-3. Axial profiles of temperature at different inlet velocities, C_3H_8 combustion.
- B-4. Axial profiles of species at different inlet velocities, C_3H_8 combustion.

Figure B-1. Axial profiles of temperature and species at different equivalence ratios, C_3H_8 combustion.

SOLID	GAS	ϕ
▼	▽	$0.19 \pm .03$
■	□	$0.22 \pm .04$
●	○	$0.25 \pm .05$
▲	△	$0.28 \pm .05$

$P_0 = 110 \pm 5 \text{ kPa}$

$T_0 = 750 \pm 14 \text{ K}$

$\langle u_1 \rangle = 15 \pm 5 \text{ m/s}$

Figure B-2. Axial profiles of temperature and species at different inlet temperatures, C_3H_8 combustion.

SOLID	GAS	$T_0(K)$
●	○	650 ± 13
▲	△	700 ± 14
▼	▽	800 ± 15

$P_0 = 110 \pm 5 \text{ kPa}$
 $\phi = 0.28 \pm 0.05$ $\langle u \rangle = 15 \pm 5 \text{ m/s}$

Figure B-3. Axial profiles of temperature at different inlet velocities, C_3H_8 combustion.

SOLID	GAS	$\langle u_i \rangle$ (m/s)
▽	▽	10 ± 4
△	△	20 ± 5
●	○	40 ± 7
$P_0 = 110 \pm 5$ kPa		
$T_0 = 750 \pm 14$ K		
$\phi = 0.30 \pm 0.07$

Figure B-4. Axial profiles of species at different inlet velocities, C_3H_8 combustion.

	$\langle u_i \rangle \text{ (m/s)}$
∇	10 ± 4
$\square$	15 ± 5
$\triangle$	20 ± 5
$\circ$	40 ± 7

$P_0 = 110 \pm 5 \text{ kPa}$
 $T_0 = 750 \pm 14 \text{ K}$
 $\phi = 0.30 \pm 0.07$