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FOSSIL FUEL COMBUSTION — 1991 —

EDITED BY
R. RUIZ



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FOSSIL FUEL COMBUSTION — 1991 —



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FOREWORD

Since the origins of mankind, combustion of fossil fuels has represented an important aspect in the development and evolution of civilization. As society has progressed, we have become more dependent on fossil fuel combustion to meet the energy requirements that our standard of living demands. Although great strides have been made by researchers and engineers over the years to utilize fossil fuel combustion in an efficient and safe manner, current concerns with energy conservation to reduce fossil fuel dependence and the impact of fossil fuel combustion on the environment have emphasized the need for additional understanding of combustion processes to develop technology that will help ameliorate these concerns.

The 1991 Fossil Fuel Combustion Symposium has provided a unique forum, attended by researchers and energy users from industry and the academic field, to address topics of current interest to the combustion community. The symposium was characterized by a good mix of relevant presentations addressing fundamental and applied research. In addition, selected experts in the combustion field were invited as guest speakers to highlight recent developments in the combustion field and address current trends and future needs.

Roberto Ruiz
Gas Research Institute
Symposium Chairman

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LEAN PREMIXED COMBUSTION FOR GAS-TURBINES: REVIEW AND REQUIRED RESEARCH

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ABSTRACT

Low NO_x regulations for stationary gas-turbines can be met by lean premixed combustion. Previous work indicates some general characteristics of NO_x in such flames, as well as some potential secondary problems.

(i) In turbulent premixed flames that are below about 1800 K, NO_x is independent of pressure, is produced by the prompt mechanism, and is largely independent of flameholder geometry.

(ii) High CO and unburned hydrocarbons leaving the flame zone must be oxidized in the turbulent post-flame gas, introducing a dependence on geometry. Two flowfield features that may quench CO in a combustor are the boundary layer flow of nonequilibrium post-flame gas over a cooled wall and the mixing of nonequilibrium post-flame gas with dilution jets. It is shown here that CO will generally burn out in either case. Hydrocarbon kinetics are more complicated, but the emissions generally track CO.

(iii) Combustor dynamics are so dependent on geometry and flow characteristics that subscale tests are of limited utility. It is not yet clear whether or not CFD can address this issue.

(iv) Materials of interest include thick durable thermal barrier coatings and all-ceramic structures. With continuous improvement, turbine inlet temperatures may eventually exceed the threshold of significant NO_x formation. There will then be a direct trade between cycle efficiency (also, inverse CO_2 emissions per unit energy output) and NO_x emissions. NO_x may be better regulated in terms of mass of NO_x per unit energy, rather than as ppm of NO_x .

(v) Modeling of turbulent combustion in realistic three-dimensional geometries is reasonably adequate for gross effects such as heat release, thermal NO_x , and combustor exit temperature profiles; it is not advanced enough to be a reliable tool for CO and UHC. Turbulence and turbulence-chemistry interaction models must be improved.

NOMENCLATURE

D	diffusivity
h	total enthalpy of mixture
N	total number of species
p	pressure
R_o	universal gas constant
T	temperature
u	axial velocity
v	transverse velocity
w	source term
W	molecular weight
x	axial coordinate
y	transverse coordinate
Y	mass fraction
λ	thermal conductivity
μ	viscosity
ν	kinematic viscosity
ϕ	equivalence ratio
ρ	density

Subscripts

n	mesh index in x-direction
j	mesh index in y-direction
k	species "k"

INTRODUCTION: WHY LEAN PREMIXED COMBUSTION IS ATTRACTIVE

Stationary gas-turbines (GT) range in size from under 10 MW to more than 150 MW. Larger units are often coupled to a heat-recovery steam-generator and a steam-turbine, yielding 200 to 250 MW capable of continuous operation for one year or more at over 50% thermal efficiency. The high efficiency may be viewed as a savings in both fuel and in CO_2 emissions, although the latter are not regulated as yet. GT-based power plants do not require much on-site construction and so can be brought on line rapidly, which contributes to their popularity. GTs fired on natural gas are in particularly great demand at present.

GT combustors traditionally operated with nonpremixed or "diffusion" flames. The resulting stoichiometric interfaces in the tur-

bulent flame lead to high NO_x (about 200 ppm NO_x at 15% O_2). To reduce the peak temperatures and thermal NO_x formation rates, water or steam is often injected into the combustors, but this is expensive in terms of process-steam or water and can have the undesirable side effects of quenching CO burnout reactions (possibly necessitating a catalyst in the exhaust), compromising stability, and leading to mechanical corrosion. Despite these difficulties, this technology is in widespread use. Optimization generally focuses on minimizing the steam or water flux for a given reduction in NO_x and requires an understanding of mixing processes in the flame. To further reduce NO_x to the levels required in some regions (e.g., 9 ppm NO_x at 15% O_2 in Southern California), ammonia-based deNO_x is implemented in the exhaust. This process has the disadvantages of adding significant capital and operating expense, as well as risking ammonia emissions. Yet another approach is rich-lean staged combustion in which a fuel-rich primary zone is followed by a lean zone to produce the correct turbine inlet temperature while, in principle, avoiding stoichiometric temperatures. Staged combustion fails the ultra-low NO_x application because it is limited by the rate at which hot rich gas can be mixed with the rest of the air to lean conditions. Nevertheless, rich-lean combustion is of interest for fuels with high fuel bound-nitrogen (FBN) levels; the rich zone converts much of the FBN to molecular N_2 rather than NO_x .

Lean premixed combustion (LPC) offers very low NO_x under GT conditions, without reducing cycle efficiency because cycle efficiency depends (for a given pressure ratio) on the turbine inlet temperature. Since turbine inlet temperatures are limited (by materials) to being below temperatures (equivalence ratios) at which NO_x is produced copiously, any high levels of NO_x are a direct result of higher equivalence ratios needed to stabilize the flame. This situation is in contrast to that of boilers, which rely on high flame temperatures to transfer heat to the walls and so intrinsically provide conditions for high NO_x . A conventional gas-turbine combustor has a nonpremixed flame with an average head-end equivalence ratio of about 1, but an exit equivalence ratio of 0.35 to 0.45, i.e., not all the air enters the flame zone. The rest enters via "dilution holes" and "film-cooling slots"; Figure 1 shows an example from the aeropropulsion field. (The net effect is not only to produce the correct bulk turbine inlet temperature but also the combustor exit temperature profile appropriate for long turbine life.) The dilution and film-cooling air are available for premixing without affecting bulk turbine inlet conditions, i.e., cycle efficiency. Thus, the fact that the flame temperature need be no higher than the turbine inlet temperature (from the cycle viewpoint; flame stability may intervene) is put to use in LPC.

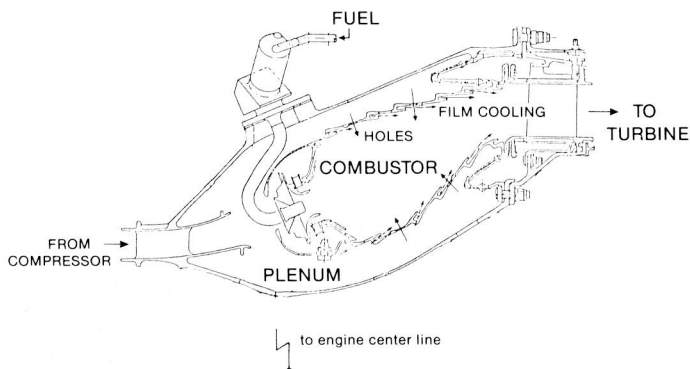


Fig. 1 Modern annular aeropropulsion gas-turbine combustor showing "dilution holes" and "film-cooling slots."

Given the limitations of alternative technologies in meeting the sub-10 ppm NO_x barrier, there has been a worldwide effort to develop LPC technology for stationary GTs (Davis and Washam, 1988). The purpose of this paper is to review progress and to indicate needs that future research in this area could address.

REVIEW OF NO_x IN LEAN PREMIXED COMBUSTION

Lean turbulent premixed flames of vaporized liquid fuel can be stabilized on a perforated plate burner, giving low NO_x emissions (Semerjian and Vranos, 1977). In practice, liquid fuels add the potential for autoignition. Much more work has been done in the area of natural-gas LPC. Sub-10 ppm levels of NO_x , an order of magnitude below NO_x in nonpremixed flames, have been demonstrated at pressures up to 10 atm in swirl-stabilized (Smith, 1987) and sudden-expansion combustors (Altemark and Knauber, 1987). Some characteristics of NO_x in high-pressure LPC are reviewed next.

The pressure-dependence of NO_x is significant in GT combustion and is also a good test of a model, potentially changing the relative contributions of different kinetic paths to NO_x . As shown below, prompt NO_x is dominant in turbulent premixed flames that are lean enough to be below 1800 K or so. There is not, however, much fundamental data on the influence of pressure. Fenimore's (1971) pioneering study of prompt NO_x , conducted in ethylene-air flames in the range $0.8 < \phi < 1.4$, $1 < p < 3$ (atm), concluded that prompt $\text{NO}_x \propto \sqrt{p}$. Later work over a wider pressure range (1 to 18 atm) concluded that prompt NO_x was independent of pressure (Heberling, 1977). Later work under GT conditions (Altemark and Knauber, 1987) also indicated that NO_x is independent of pressure below $\phi = 0.6$.

More recently, NO_x in turbulent premixed methane-air flames was studied using an uncooled perforated-plate burner operating at pressures from 1 to 10 atm, inlet air temperatures from 300 K to 615 K, and equivalence ratios from 0.5 to 0.9 (Correa, 1989a; Leonard and Correa, 1990). Modeling employed a stirred reactor for flame stabilization followed by a plug flow reactor and a kinetic scheme, which included thermal and prompt NO_x , but not C_2 chemistry (Glarborg et al., 1986). Figure 2 presents NO_x at 10.4 atm, with the inlet air temperature as a parameter. These data are very similar to others obtained with different means of flame stabilization. The calculations (solid lines) compared well with the data over the entire range of parameters and indicated that the low temperatures of lean flames preclude significant formation of NO_x by the thermal mechanism. The prompt NO_x mechanism is dominant below about 1800 K; this is also evident in the sensitivity analysis by Glarborg et al. (1986). Figure 3 compares data and calculations of NO_x at 322 K inlet temperature, with pressure as a parameter. NO_x varies as \sqrt{p} in the near-stoichiometric premixed flames, as is observed in nonpremixed flames where most of the NO_x is formed in near-stoichiometric interfaces via the thermal mechanism. NO_x is independent of pressure in the leanest premixed flames (Fig. 3).

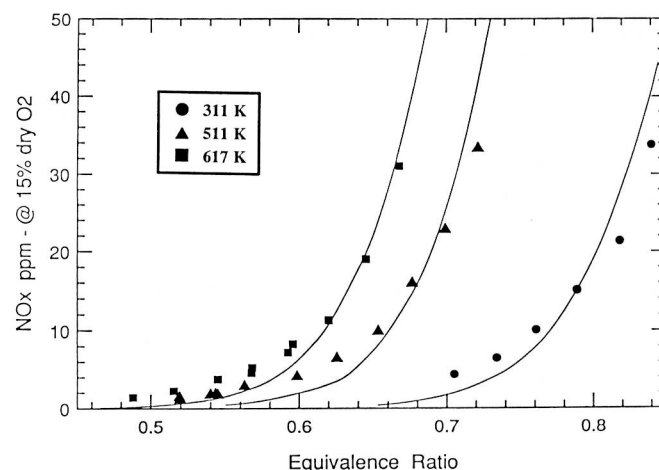


Fig. 2 Measured and predicted NO_x at 10.4 atm with inlet air temperature as a parameter.

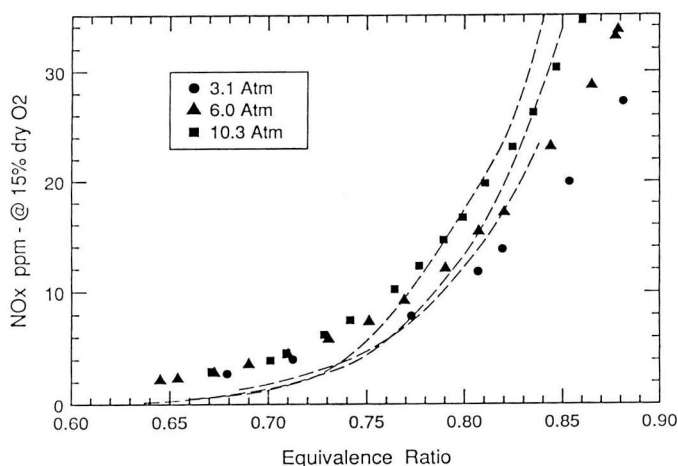


Fig. 3 Measured and predicted NO_x at 322 K inlet temperature with pressure as a parameter.

A companion numerical study of fifteen laminar premixed methane-air flames (Correa and Smooke, 1990) used the Miller-Bowman scheme (1989) in the range of pressure 1 to 10 atm and equivalence ratio 0.6 to 1.0, and provided the sensitivity of NO and NO_2 to the rates of all reactions and to pressure. The main conclusions were that (i) thermal NO_x dominated in the near-stoichiometric flames, (ii) the $\text{N}_2 + \text{O} + \text{M} = \text{N}_2\text{O} + \text{M}$ mechanism was influential in lean flames (Fig. 4), unlike the above turbulent flames, and (iii) NO_x was independent of pressure in the leanest laminar flames (Fig. 5), as in the above turbulent flames. Together with sensitivity analyses for stirred reactors, such results indicate critical steps in the prompt NO_x and N_2O pathways. Note that some of the rate constants have not been established definitively. For example, the activation energy for the key prompt NO_x reaction $\text{CH} + \text{N}_2 = \text{HCN} + \text{N}$ has recently been measured (Dean et al., 1990) as approximately 22 kcal/mol rather than 14 kcal/mol, which is widely used (Miller and Bowman, 1989). Such uncertainty affects the prediction of NO_x once the flame is outside the thermal NO_x regime. Differences between the laminar and turbulent flames are also of importance, both in interpretation of data and in modeling.

Previous work (Kramlich et al., 1987), which implicated N_2O as a significant emission of coal combustion, has been revised to show that N_2O was an artifact of the measurement (Muzio et al., 1990). Likewise, N_2O is not significant in natural-gas fueled turbines. Another role for N_2O is as an intermediate in NO_x production: low-temperature fixation of nitrogen by $\text{N}_2 + \text{O} + \text{M} = \text{N}_2\text{O} + \text{M}$, followed by conversion of N_2O to NO, has been seen in studies of lean laminar premixed flames of CH_4 (Correa and Smooke, 1990) and C_2H_6 (Drake et al., 1990).

CO: A PROBLEM AT THE LIMITS OF CFD

It is more difficult to characterize CO than NO_x in a turbulent flame. The reason is that thermal NO_x chemistry (the cause of high NO_x levels) is too slow to interact with the fine-scale turbulence, in lean premixed flames (Correa, 1989b). On the other hand, CO chemistry can interact with the Batchelor/Kolmogorov scales. Even though CO oxidation is simple kinetically—the only significant route being $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ (Cherian et al., 1981)—a complete theory for CO is handicapped by the lack of mathematically tractable theories for small-scale turbulence in complex flows.

Why is CO an issue? CH_x species in the flame stabilization zone react rapidly (faster than CO) with oxidizing radicals. Thus CO cannot be oxidized until the fluid exits the stabilization region and the CH_x levels drop. Levels of 300-ppm CO and 30-ppm UHC or higher

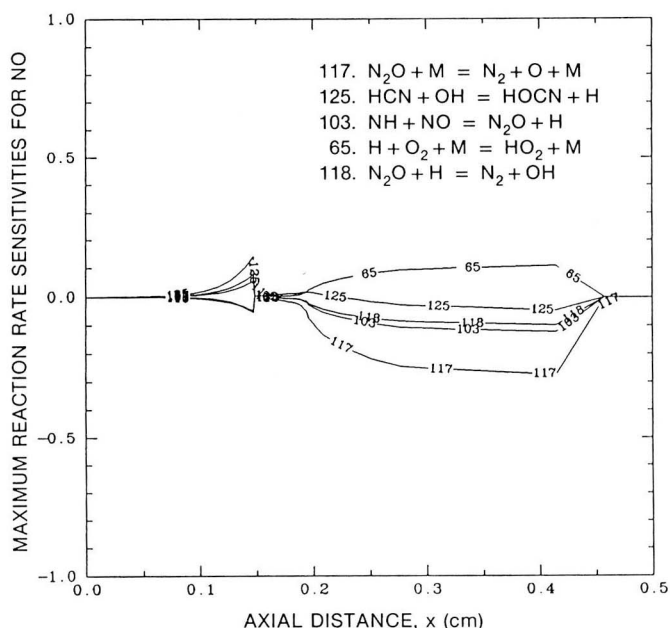


Fig. 4 Top sensitivity coefficients in atmospheric laminar $\phi = 0.6$ flame showing influence of $\text{N}_2 + \text{O} + \text{M} = \text{N}_2\text{O} + \text{M}$.

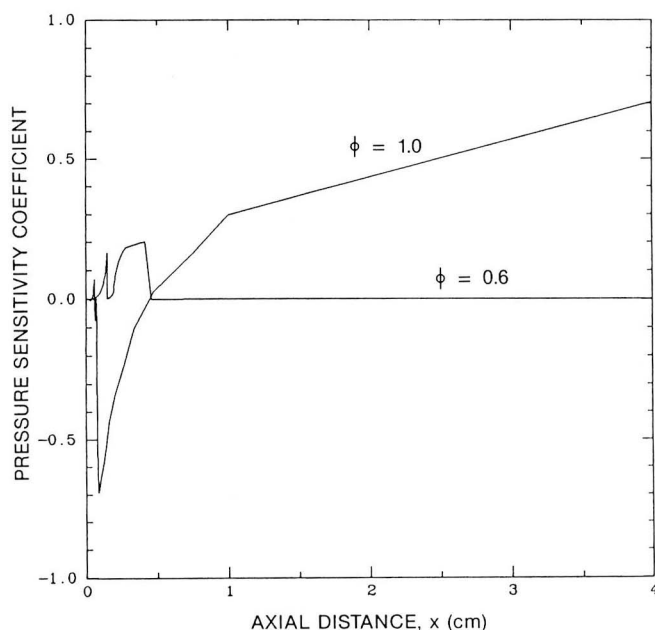


Fig. 5 Pressure sensitivity in atmospheric laminar $\phi = 0.6$ flame.

(functions of ϕ and flow parameters) may be expected to survive the primary flame and must be oxidized ($\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$) in the turbulent post-flame gas, introducing a critical dependence on the geometry and air addition schedule. Moreover, direct measurement of CO in the stabilization region is difficult: a sampling probe cannot provide the cooling rate required to quench CO ($1\text{--}3 \times 10^6$ K/s for an initial temperature of 1800 K) and so CO sampled in the flame itself burns out in the sampling line. On the other hand, high cooling rates are indeed experienced in turbine passages and freeze CO at combustor exit values. Two potential modes of CO quenching are investigat-

ed here: (i) boundary layer flow over cooled walls and (ii) turbulent mixing with air.

(i) **CO oxidation over cooled walls:** The rate of CO oxidation is reduced by two-to-three orders of magnitude between flame-like (1800 K) and combustor liner-like (1100 to 1200 K) conditions: can this reduction quench CO in boundary layer flow?

The model (Correa, 1990a) starts with a stirred reactor computation of the flame stabilization zone. The conditions of 19 atm, inlet temperature 710 K, and equivalence ratio 0.5 yield a flame temperature of about 1800 K along with the velocity, density, and species mass fractions. Initial conditions are taken as plug flow at these conditions. The freestream boundary condition is the same velocity but at the equilibrium post-flame composition and temperature (Fig. 6). The wall temperature is taken as 1100 K. The numerical method and chemical scheme are outlined in the Appendix. Eddy viscosity and diffusivity were taken as 200 x laminar values, for convenience. Inert flow calculations were checked, and they agreed with the Blasius profiles.

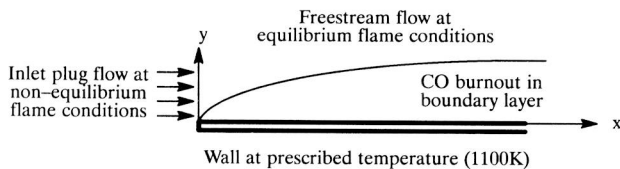


Fig. 6 The cool-wall boundary layer problem of CO burnout.

Figure 7 shows the transverse profiles of axial velocity, temperature, and CO at a position $x = 0.3$ m, representative of a practical combustor length. The CO kinetics are fast enough to track equilibrium despite the mass transport. Figure 8 shows that despite the reduction of CO oxidation rate with temperature, CO burns out rapidly along the wall.

These results for CO oxidation are consistent with related studies available in the literature. Khitrin and Solovyeva (1958) studied the combustion of CO in air saturated with water vapor, using heated 15 x 0.2 cm² quartz tubes. The velocity of the premixed flow was varied between 1 and 34 m/s, the latter approaching the regime of interest here. At the the highest tube temperature of 1200 K, the 34 m/s flow had experienced ~80% oxidation of the CO by the end of the tube. These data qualitatively support the present findings. A more recent numerical study of the catalytic combustion of a mixture of 4% CO, 20% O₂, and 76% N₂ showed that above 1150 K, homogeneous oxidation dominated the process (Harrison and Ernst, 1978). These results appear to confirm that above 1100 to 1200 K, the CO in boundary layers is substantially oxidized by homogeneous-phase reactions. Since wall temperatures of 1100 K are attainable in present gas-turbine combustors, CO ought to be oxidized.

Westbrook et al. (1981) analyzed the quenching of laminar flames of methane and methanol at cold walls, looking for a potential source of unburned hydrocarbons in spark-ignition engines. Their results include one-dimensional computations of a flame propagating towards a 300-K wall through a stoichiometric CH₄-air mixture at a pressure of 10 atm. Because of the high pressure, the flame speed is only about 14 cm/s, and the flame was quenched when it approached to within about 0.1 mm of the wall. Quenching occurred as a result of the rapid radical recombination at the low temperatures near the wall; such reactions are faster at lower temperatures and compete with chain-branching reactions for the available radical pool, eventually quenching the flame. The quenching distance was about 0.2 mm in a $\phi = 0.7$ flame. Even after the flame was quenched, however, the remaining species rapidly diffused away from the wall and were oxidized. Clearly, much greater transport rates are required for species to be quenched and to be maintained at cold walls.

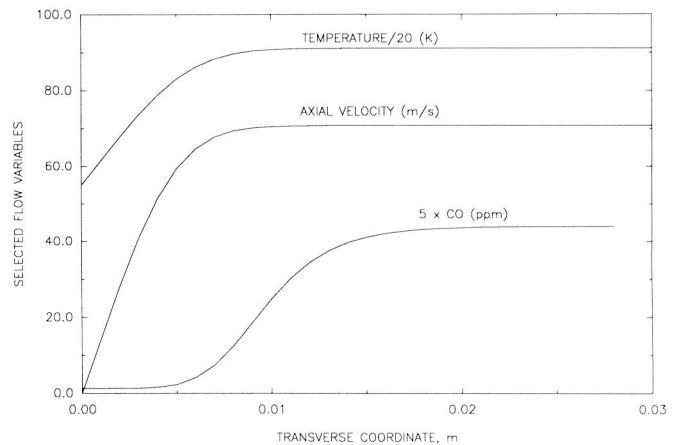


Fig. 7 Transverse profiles of axial velocity, temperature, and CO at axial station $x = 0.3$ m.

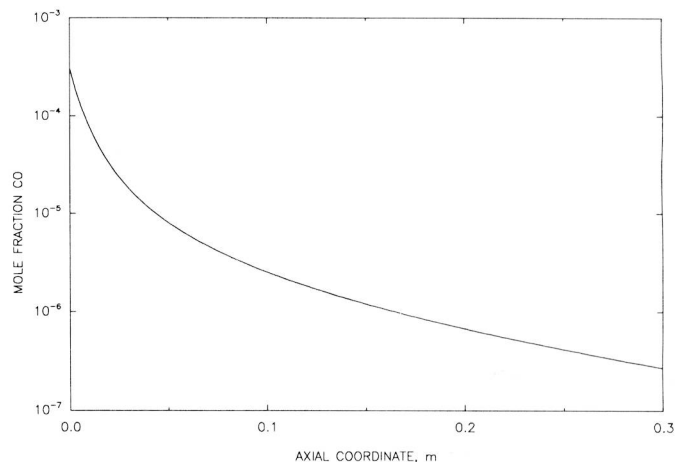


Fig. 8 Rapid burnout of post-flame nonequilibrium CO along 1100 K wall.

Thus CO is in fact oxidized in the wall boundary layers because the transverse transport rates (convection-plus-turbulent diffusion) are not high enough for the rate reduction with temperature to be significant, i.e., high-CO gas continues to oxidize (to local equilibrium) on its way across the boundary layer (Correa, 1990a).

(ii) **CO oxidation in turbulent eddies:** Another phenomenon that could potentially quench CO oxidation is rapid turbulent mixing between hot high-CO gas and air (dilution) jets at compressor discharge temperature. Mixing and cooling are carried out by convection and diffusion at scales down to those of the dissipative processes of turbulence. Can these processes produce cooling rates high enough to quench CO in turbulent eddies in the post-flame gas? The turbulent eddies having the highest strain (mixing rates) are those on the ~ 100 μ m Kolmogorov scale. Since turbulence on this small a scale cannot be addressed by CFD (computational fluid dynamics), a model for CO oxidation in an isolated eddy is used for demonstration. Consider turbulent mixing as the flow into an eddy in a Lagrangian frame (Fig. 9). The model (Correa, 1990b) is based on the unsteady one-dimensional strained diffusion equation for concentration c (here that of CO), which describes flow at these scales:

$$\frac{\partial c}{\partial t} - a(t)x \frac{\partial c}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) + w \quad (1)$$

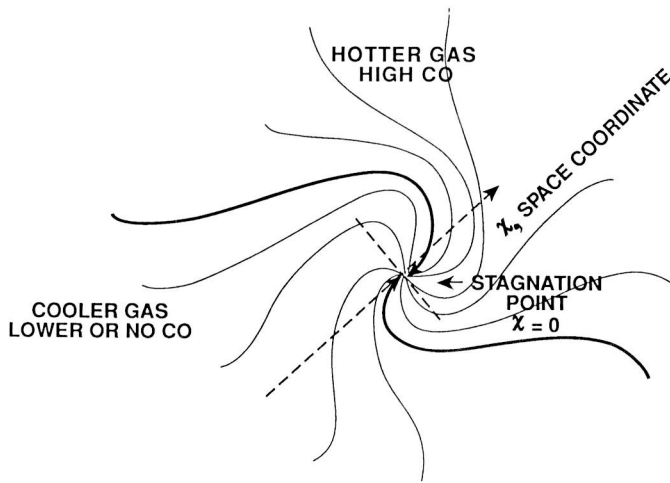


Fig. 9 The problem of CO burnout in a turbulent eddy.

The terms in Eq. (1) have the following physical interpretations:

(a) the transient term describes the evolution of this stagnation point flow as the strain rate $a(t)$ varies.

(b) the strain-rate $a(t)$ varies as the eddy is stretched by turbulence; the convection is towards the stagnation point $x = 0$ from either side and is proportional to $|x|$. Cases with $a(t)$ constant and $a(t)$ varying with time are considered in turn in Correa (1990b).

(c) the diffusion term describes laminar transport. The diffusivity is a function of temperature and pressure, taken as D (in m^2/s) = $1.6 \times 10^{-5} (T/300)^{1.8} / p$, where T is Kelvins, and p is atmospheres.

(d) the source term describes chemical reaction.

The burnout of trace amounts of CO releases little heat, and so the corresponding temperature equation is homogeneous:

$$\frac{\partial T}{\partial t} - a(t)x \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left(\alpha \frac{\partial T}{\partial x} \right) \quad (2)$$

The thermal diffusivity α follows from an assumption of unity Lewis number, although the latter is not necessary for solution of the equations since a numerical technique is used. The chemical reaction rate, w in Eq. (1), is modeled in a simple manner for convenience; only the forward rate is considered, and the OH levels are taken from nonequilibrium stirred reactor calculations. This simplification makes the governing equations above self-complete, without the need for additional species equations. The equations are solved by an implicit finite-difference method, which is first-order accurate in time and second-order accurate in space.

Boundary conditions are (i) mass fraction $Y_{\text{CO}} = 300 \times 10^{-6}$ and $T = 1800$ K at $x = L/2$, simulating hot CO-bearing post-flame gas; L is taken as 1 mm, larger than the Kolmogorov scale; and (ii) $Y_{\text{CO}} = 50 \times 10^{-6}$ and $T = 900$ K at $x = -L/2$, representing gas in a state intermediate between the post-flame gas and the compressor discharge air. The initial condition on each variable is a linear function between the boundary values. The equations are solved numerically on a 51-point mesh, with a time step of $0.001/a$ (Correa, 1990b). After nondimensionalizing Eqs. (1) and (2), two parameters are seen to govern the behavior of the system: $L^2 a/D$, which is in effect a Peclet number, and $(k_f)(c)/a$, which is in effect a Damkohler number; here D , k_f , and c are characteristic diffusivities, forward reaction rates and OH concentrations, respectively. These parameters compare the effects of convection, via the strain “ a ,” on diffusion and reaction, respectively. Characteristic scales expected in the problem can also be obtained. The initial concentration profile will relax to the time-asymptotic

(“steady”) state in a time of order $1/a$ under the influence of convection and a time L^2/D under the influence of diffusion; the latter time scale is much larger and therefore not relevant for the large Peclet numbers generally of interest here. On the other hand, the Peclet number goes to zero as $|x|$, since the convective velocity is $[-a(t)x]$. Thus diffusive effects dominate near the stagnation point $x = 0$. In the steady state, the thickness of the strained diffusion layer is on the order of $\sqrt{D/a}$.

Figure 10 shows the evolution of CO and temperature for $a = 500 \text{ s}^{-1}$. The CO burns out more rapidly in the hotter gas. On the other hand, on the cool side (left side), CO is convected towards $x = 0$ without being oxidized, i.e., it is quenched. Is this quenching a serious issue? Calculations for other cases show that this hypothetical intermediate state (50 ppm, 900 K) could not occur in the course of post-flame turbulent mixing. If, however, unburned fuel-air mixture escaped the primary flame stabilization zone and pyrolyzed to high CO levels downstream, such high-CO cool conditions could be realized.

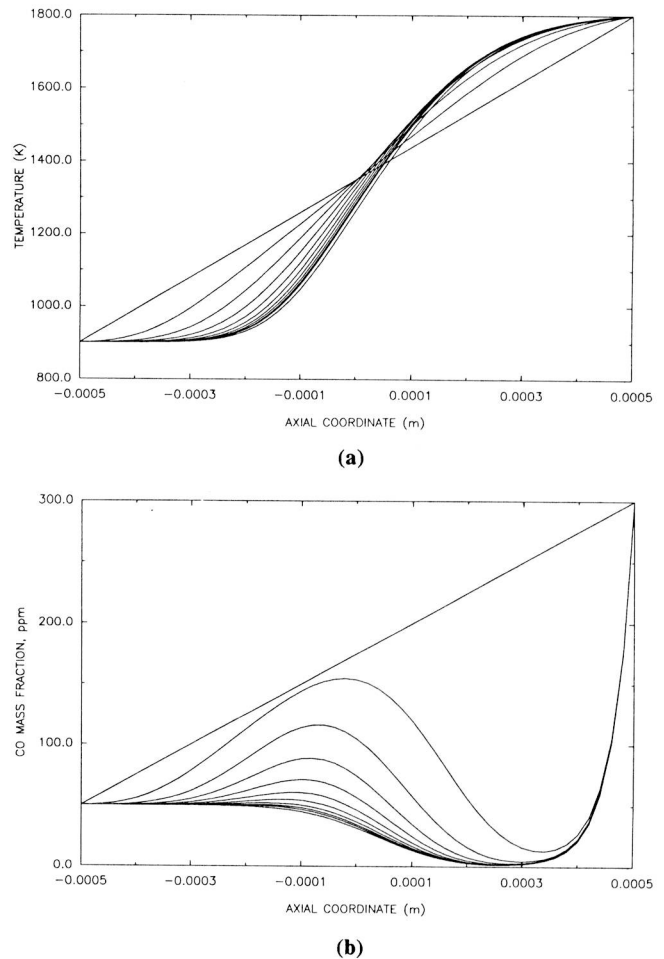


Fig. 10 Transient evolution of (a) temperature and (b) CO for a strain of 500 s^{-1} . Spacing between curves is $2/3 \text{ ms}$.

Reliable methods for measurement of CO in the ~ 100 -ppm range in high-temperature nonequilibrium gases are not available. Physical probes cannot cool the gases rapidly enough to quench CO sampled in the flame, and so the CO equilibrates to some low-temperature level. Nonintrusive techniques may offer a way forward. Hanson (1986) reviewed two-photon laser-induced fluorescence of CO in CO-air diffusion flames and concluded that the technique would become use-

ful to combustion diagnostics. Another interesting approach is monitoring the variation in the conductance of a (tin dioxide) semiconductor as CO-bearing gas flows over the surface (Harkoma, 1988); this sensor was intended to monitor CO in utility applications where interference from NO had to be tolerated.

DYNAMICS AND FLAME STABILITY

Perhaps the most influential nonemissions issue in stationary GTs is that of turndown. In a nonpremixed combustor, turning down the fuel flow for part-load operation will simply lead to a smaller flame zone. In LPC, however, the combustor may already be near its lean limit. Reduced fuel flow can be tolerated by using techniques such as (i) designing the combustor to have a number of independent burners, and then shutting off the fuel to some of these ("fuel-staging"), (ii) redirecting some of the premixing air to the latter part of the combustor to maintain the flame equivalence ratio above the blowoff limit ("air-staging"), (iii) shifting into a nonpremixed mode, at the expense of emissions. Techniques requiring moving parts are less attractive in practice.

Many interesting problems are provided by the unsteady aspects of bluff-body stabilized premixed flames. Different dynamic regimes appear as the mixture is leaned to blowoff. Consider first the near-stoichiometric case, which is also of interest in afterburners for military jet engines; in the laboratory the frequency of the fluctuations often corresponds to a quarter longitudinal wave upstream of the flame-holder. One-dimensional models that relate the unsteady heat release to the unsteady velocity fluctuation through a chemical induction time are quite successful in predicting the longitudinal modes. Strouhal shedding may be excited and may amplify the pressure fluctuations. (In practice, much higher frequencies associated with radial or circumferential modes may be dominant.) Near the lean blowoff limit, lower frequencies associated with bulk (Helmholtz) modes may dominate. These dynamic characteristics depend heavily on the flame-holder and combustor geometries, and on the flowfield. Sub-scale testing is of limited utility. It will be interesting to see if unsteady CFD such as the discrete vortex model (Ghoniem, 1986) can account for dynamics and stability, and perhaps quantify the relative roles of shedding and acoustics as a function of the equivalence ratio (load).

MATERIALS

Material limits affect emissions in two ways. Recall that the minimum temperature within the combustor must be that at the turbine inlet (say, T_i), which at present is below the threshold of significant NO_x formation (say, T_{NO_x}). As materials permit higher combustor wall temperatures, it will be possible to use progressively less cooling air for the liner. The extra air may be premixed, leaning out the flame to the T_{NO_x} threshold unless the lean stability limit intervenes. Such materials technology lies in thick durable thermal barrier coatings and in all-ceramic structures. Techniques for lean flame stabilization and for liner cooling with limited air will be critical.

As materials permit higher turbine inlet temperatures, T_i may eventually exceed T_{NO_x} and there will be a direct trade between cycle efficiency (also, inverse CO_2 emissions per unit energy output) and NO_x emissions. The trade may be made more obvious by regulating NO_x in terms of mass of NO_x per unit energy, rather than as mole fraction (ppm) of NO_x .

MODELING

Modeling of gas-turbine combustors must account for turbulent flames in realistic three-dimensional geometries, including finite-rate chemistry and radiation, but not for spray phenomena except in unusual circumstances; of course, the latter point is moot for LPC. Nonorthogonal body-fitted curvilinear grid generation followed by coordinate transformation allows complex three-dimensional geometries to be "meshed." Modern numerics are reducing (but have

not yet eliminated) the artificial viscosity introduced in discretization of high Reynolds number convection terms (Correa and Shyy, 1987). On the negative side, the averaged Navier-Stokes equations are most often used and are closed with gradient-diffusion (e.g., $k-\epsilon$) or Reynolds stress/flux models. Moreover, turbulence-chemistry interactions are usually closed with assumed shape pdf's (with lower moments from balance equations). This class of models is reasonably adequate for gross effects such as heat release, thermal NO_x , and combustor exit temperature profiles; it is not advanced enough to be a reliable tool for CO and UHC, which interact with the fine scales of turbulence. Turbulence and turbulence-chemistry interaction models must be improved or replaced, perhaps with the Monte-Carlo/pdf approach (Pope, 1990). Additionally, prediction of emissions will require computationally tractable simplifications of the chemistry (Bilger and Kee, 1987). Unsteady models (Ghoniem, 1986) are needed to account for dynamics and stability in premixed combustion.

CONCLUSIONS

Gas-turbines for heavy-duty continuous stationary power generation have the advantages of rapid delivery times, high efficiency in the combined cycle mode, and the potential for very low emissions. Lean premixed combustion is probably the only combustion technology that will provide sub 10-ppm NO_x levels, at least in the immediate future. Catalytic combustion is still not available from the materials point of view. NO_x in LPC depends primarily on flame temperature, not flame-holder geometry or pressure, and is predicted quite well by relatively simple models such as stirred/plug flow reactors. Some rationalization is provided by the discussion of Correa (1989b). Even for thermal NO_x , superequilibrium in the radical pool broadens the NO_x formation zone, replacing the narrow flamelet-like structure expected of a high activation energy reaction (Peters, 1987) with a distributed reaction zone (Bilger, 1988). N_2O is not emitted in significant quantities. Large amounts of CO are produced in the stabilization zone of a lean premixed flame and must be oxidized in the turbulent post-flame gas. Unlike NO_x , CO can therefore depend on the flame-holder shape and the turbulent post-flame flowfield. In the general case of nonequilibrium flame gas flowing over cooled walls or being turbulently mixed with dilution air, however, the CO continues to oxidize. Emissions of UHC are more complicated kinetically, but generally track CO. Dynamics and flame stability are strongly dependent on geometry. Oscillation modes are of the Helmholtz (bulk) and longitudinal variety in laboratory tests, with transverse modes or system interactions often dominating in practical cases.

LPC deprives the latter part of the combustor of air. In the limit, film-cooling of the liner may no longer be possible. This is motivating work on advanced liner cooling concepts and on materials such as thermal barrier coatings and all-ceramic structures. In the limit of very high-temperature materials becoming available, the turbine inlet temperature may exceed the threshold of significant NO_x -formation. At that point, NO_x reductions will be obtained only at the expense of cycle efficiency.

Modeling of turbulent combustion in realistic three-dimensional geometries is not advanced enough to be a reliable tool for all the quantities of interest. The prevalent $k-\epsilon$ /assumed shape pdf closure model (Correa and Shyy, 1987) must be improved or replaced, perhaps with the Monte-Carlo/pdf approach (Pope, 1990). Prediction of emissions will require computationally tractable simplifications of the chemistry (Bilger and Kee, 1987) and suitable turbulence-chemistry interaction models. Unsteady models (Ghoniem, 1986) are needed to account for dynamics and stability in premixed combustion.

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APPENDIX

Finite-Difference Model

A numerical finite-difference model of the boundary-layer Navier-Stokes equations [Schlichting (1979)], including chemical reactions, is developed [Correa (1990a)]. The equations consist of continuity:

$$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) = 0 \quad (1)$$

axial momentum:

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} + \frac{\partial p}{\partial x} = \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (2)$$

total enthalpy, which is defined for the low Mach number flows of interest here as the sum of the sensible enthalpy and the enthalpies of formation, and so is invariant under chemical reaction:

$$\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} = \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right) \quad (3)$$

the mass-fractions Y_k of N species:

$$\rho u \frac{\partial Y_k}{\partial x} + \rho v \frac{\partial Y_k}{\partial y} = \frac{\partial}{\partial y} \left(\rho D \frac{\partial Y_k}{\partial y} \right) + w_k \quad k=1,N \quad (4)$$

and the equation of state:

$$p = \rho R_o T / \bar{W} \quad (5)$$

where the overbar refers to mixture-averaged properties. The heating due to viscous dissipation is neglected in Eq. (3) because it is small compared with the difference in thermal energy between the freestream and the plate [Schlichting (1979)]. That viscous dissipation is negligible was also shown by retaining these terms and reproducing the Blasius result (which ignores the energy equation altogether), for the freestream velocities of interest here.

Transport properties (viscosity, thermal conductivity, mass diffusivity) are taken as constant. A constant turbulent eddy viscosity is used in the numerical examples. It is straightforward to introduce properties as functions of temperature, or as functions of turbulence quantities determined from additional conservation equations, but such calculations cannot easily be checked. Moreover, allowing for variation of properties is unlikely to change the conclusions in a significant way.

The governing equations (1)-(5) are solved by a numerical finite-difference method. The procedure consists of,

(i) first solving Eq. (2) for u , Eq. (1) for v , and Eq. (3) for h , with other variables lagged from a previous step,

(ii) then setting up the convective and diffusive fluxes of Y_k into each control volume, and using the implied atomic mass fraction inputs with the local enthalpy h to solve for the Y_k and temperature T subject to the chemical kinetics of Table I,

(iii) iterating between (i) and (ii) to convergence on temperature at each point in a given axial plane before marching to the next plane. The details follow.

Discretization of the equations is first-order in the axial direction, and second-order (central differences) in the transverse direction. The convective coefficients are lagged from the previous axial plane [Andersen et al. (1984)]. Discretization of the axial momentum equation (2) results in the algebraic equation,

$$\rho_j^n u_j^n \frac{u_j^{n+1} - u_j^n}{\Delta x} + \rho_j^n v_j^n \frac{u_{j+1}^{n+1} - u_{j-1}^{n+1}}{2\Delta y} = \mu \frac{u_{j+1}^{n+1} - 2u_j^{n+1} + u_{j-1}^{n+1}}{\Delta y^2} - \frac{\partial p}{\partial x} \quad (6)$$

Table 1

Methane Pyrolysis Mechanism

$k_f = 10^a T^n \exp(-T_a/T)$, SI units

			a	n	T_a	
1.	$\text{CH}_4 + \text{O}_2$:	11.5	0.0	12200.	GLOBAL STEP
2.	$\text{H} + \text{O}_2$	=	13.71	-0.82	8309.	
3.	$\text{O} + \text{H}_2$	=	7.26	1.0	4444.	
4.	$\text{H}_2 + \text{OH}$	=	6.08	1.3	1827.	
5.	$\text{OH} + \text{OH}$	=	5.78	1.3	0.0	
6.	$\text{H} + \text{OH} + \text{M}$	=	18.88	-2.6	0.0	
7.	$\text{O}_2 + \text{M}$	=	8.28	0.5	48093.	
8.	$\text{H} + \text{H} + \text{M}$	=	13.0	-1.0	0.	
9.	$\text{H} + \text{O}_2 + \text{M}$	=	13.32	-1.0	0.0	
10.	$\text{HO}_2 + \text{H}$	=	10.4	0.0	352.2	
11.	$\text{HO}_2 + \text{H}$	=	11.4	0.0	956.2	
12.	$\text{HO}_2 + \text{O}$	=	10.68	0.0	503.	
13.	$\text{HO}_2 + \text{OH}$	=	10.7	0.0	503.	
14.	$\text{O} + \text{O} + \text{M}$	=	8.51	0.0	-2113.	
15.	$\text{CO} + \text{O}_2$	=	9.4	0.0	24006.	
16.	$\text{CO} + \text{OH}$	=	4.18	1.3	-385.	
17.	$\text{CO} + \text{HO}_2$	=	10.76	0.0	11540.	

where the superscripts “n” and “n+1” refer to the previous and current axial planes, respectively, and the subscripts “j-1” and “j” refer to the previous and current transverse points, respectively. The implicit formulation is used to enhance numerical stability and permit larger steps in the axial direction. The axial pressure gradient $\partial p / \partial x$ is prescribed. Eq. (6) may be recast into a tridiagonal matrix form [Andersen et al. (1984)], and solved by the tridiagonal matrix algorithm (TDMA).

The transverse velocity v is obtained from the continuity equation. In discretized form, this yields

$$\frac{\rho_{j+1}^{n+1} u_{j+1}^{n+1} - \rho_{j+1}^n u_{j+1}^n + \rho_j^{n+1} u_j^{n+1} - \rho_j^n u_j^n}{2\Delta x} + \frac{\rho_j^{n+1} v_j^{n+1} - \rho_{j-1}^{n+1} v_{j-1}^{n+1}}{\Delta y} = 0 \quad (7)$$

This equation can be recast into an explicit equation for v_j^{n+1} in terms of known quantities. It is solved starting at the wall where $v = 0$ and marching outwards to the freestream. The transverse velocity obtained in this way is a consequence of the “displacement thickness” of the boundary layer.

The discretized enthalpy equation is similar to Eq. (6) except that the conduction term is not implicit,

$$\rho_j^n u_j^n \frac{h_j^{n+1} - h_j^n}{\Delta x} + \rho_j^n v_j^n \frac{h_{j+1}^{n+1} - h_{j-1}^{n+1}}{2\Delta y} = \lambda \frac{T_{j+1}^n - 2T_j^n + T_{j-1}^n}{\Delta y^2} \quad (8)$$

Again Eq. (8) may be solved by the TDMA, with the conduction term considered to be explicit.

An alternative formulation of Eq. (3), in terms of temperature T rather than enthalpy h , would permit an implicit conduction term but also add highly nonlinear Arrhenius source terms. The use of h as the dependent variable allows simultaneous determination of the tempera-

ture and species’ mass fractions by the same solver. This strategy is necessary for convergence in kinetically complex systems where the greatest nonlinearities are chemical rather than hydrodynamic [Pratt and Wormeck (1976)].

Finally, the conservation equation for the species “k” ($k = 1, N$) is

$$\rho_j^n u_j^n \frac{Y_{k,j}^{n+1} - Y_{k,j}^n}{\Delta x} + \rho_j^n v_j^n \frac{Y_{k,j+1}^{n+1} - Y_{k,j-1}^{n+1}}{2\Delta y} = \rho_{j+1/2}^n D(Y_{k,j+1}^{n+1} - Y_{k,j}^{n+1}) - \rho_{j-1/2}^n D(Y_{k,j}^{n+1} - Y_{k,j-1}^{n+1}) + w_{k,j}^{n+1} \quad (9)$$

With the atomic ratios and the enthalpy from Eqs. (8) and (9), an auxiliary set of chemical (inert, equilibrium or kinetic) calculations is performed. The new temperature and species mass-fractions are returned at each grid-point and the iterative process continued to convergence on the temperature (typically 3 K deg.). All the calculations are performed on a Cartesian grid. Calculations of inert flow agreed with Blasius profiles [Correa (1990a)].

Kinetics

Earlier numerical studies of NO_x formation used complete methane oxidation schemes, including CH_x ($x = 1, 4$) and aldehyde chemistry, and the relevant N-species (HCN , NH_x ($x = 1, 3$), etc.) in thermal and prompt NO_x . In the present study, however, only the CO and the subsequent burnout are of interest and so a pyrolysis scheme is used (Table I). In this scheme fuel is converted at some global rate to CO and H_2 , which then burn out simulating the problem of present interest. Such schemes have also been used to simulate liquid-fueled gas-turbine combustors, since full schemes are not available for higher hydrocarbons [Kauffman et al. (1982)]. The global pyrolysis step is followed by details of CO oxidation (Table I).

Note that each computational cell is in effect a stirred reactor. These cells are connected by the convective and diffusive fluxes implied by the Navier-Stokes equations. Since the number of cells is large, the pyrolysis scheme effects a significant computational savings.

PRELIMINARY TESTS OF FUEL-BOUND NITROGEN CONVERSION USING NITROGEN-DOPED DIESEL FUEL IN A SINGLE-CYLINDER DIESEL ENGINE

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ABSTRACT

It is assumed by many that NO_x from coal-fueled engines may be largely derived from the high concentration of fuel-bound nitrogen (1.2% to 2.0%) in the coal feedstock. Conversion of fuel-bound nitrogen to NO_x during combustion in a single-cylinder direct-injected research diesel engine was investigated by doping a No. 2 diesel fuel with nitrogen-containing organic compounds. The base fuel was a standard research grade No. 2 diesel fuel doped with quinoline ($\text{C}_9\text{H}_7\text{N}$) to levels of 1 and 2% nitrogen by mass. Quinoline was chosen as the primary nitrogen additive based on, among other things, its similarity to nitrogenous compounds contained in coal-based fuels. The results showed an increase in NO_x emissions with additive concentration. The percent of nitrogen converted was independent of additive concentration in the concentration range of 1 to 2%. Conversion exhibited a weak but statistically significant relationship with load and speed. Fuel-bound NO_x conversion appeared to increase with speed and decrease with load. Overall conversion rates were lower than anticipated (< 20% on average) and may possibly be attributed to the diffusion controlled combustion process inherent to diesel engines and to the fuel nitrogen chemistry itself.

INTRODUCTION

Emissions of NO and NO_2 , collectively referred to as NO_x , are an issue in the development and utilization of coal-fueled diesel engines (McMillian and Webb 1989). Although a proportion of the NO_x emissions from combustion of coal or coal-based fuels is due to oxidation of atmospheric nitrogen (thermal NO_x), a significant portion could be derived from the combustion of nitrogenous compounds in the fuel. A series of baseline tests were conducted in a single cylinder diesel engine using standard diesel fuel doped with nitrogen additives to simulate the combustion of nitrogenous compounds contained in coal and coal-derived fuels. The purpose of these tests were to provide a baseline for subsequent investigations in fuel-bound nitrogen conversion as functions of fuel chemistry and injection parameters.

The diesel engine is a relatively complex heat engine whose emission characteristics not only depend on the engine operating parameters and working fluid properties but also on combustion chemistry. For this reason a standard carrier fuel, diesel fuel No. 2, was chosen as the carrier for the fuel-bound nitrogen compounds. The quantities of nitrogenous additives in the diesel fuel were such that, besides supplying nitrogen to the fuel, they were assumed to play a theoretically insignificant part in the combustion process in that combustion temperature, combustion rates and ignition delay were not altered and thus were not expected to convolute the resultant emissions levels. It turned out that ignition delay etc. were not affected, however, resultant emission levels may be suspect due to additional aromatic loading of the fuel. The effects on emissions will be discussed later. The fuel combination was also chosen because the levels of fuel bound nitrogen were easy to control.

Most laboratory analytical experiments in NO_x emissions have focused on NO formation alone and not on NO_2 (Glassman, 1987). NO_2/NO_x ratios have been seen to increase under fuel lean conditions. Under fuel lean conditions significant amounts of NO may be converted to NO_2 by several mechanisms including $\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$. Although diesels operate very fuel lean, most of the overall NO_x emissions is NO .

NO_x formation mechanisms may be classified by "thermal", "prompt" or "fuel-bound" NO_x . NO_x formation from fuel-bound nitrogen is meant to specify the NO formed from fuel compounds that contain nitrogen atoms bound generally to carbon or hydrogen. These compounds include ammonia, pyridine, quinoline, their derivatives as well as nitrogenous organic compounds with three or more ring structures. NO_x from the thermal mechanism has been thoroughly studied in many combustion systems including diesels (Wu and Peterson, 1986) and (Heywood, 1988).

NO_x emission levels from combustion systems using fuel-bound nitrogen containing fuels have been shown to be higher than levels from combustion systems operating on fuels without nitrogen (Schultz and Wolfbrandt,