

# The Role of Coal Devolatilization in Comprehensive Combustion Models

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## Introduction

Pulverized coal combustion is a complex interaction of several processes, including particle dispersion, gas-phase mixing, particle heatup and mass transfer, particle and gas reactions, recirculating and swirling fluid mechanics, radiative heat transfer, mineral matter phase transformations, and pollutant formation and destruction. Comprehensive models which include submodels for many of these processes have been developed by several investigators (1-4) to predict local conditions inside combustors. This paper focuses on the role of coal devolatilization submodels in such predictions.

Previously reported studies of the effects of devolatilization kinetics on overall combustor characteristics have demonstrated that combustion efficiency, flame front location, and fluid dynamical structure, are all sensitive to devolatilization rate over the range of published values (5). Similar effects were noted in this study. Based on these findings, the rate of mass evolution during devolatilization is considered to be important to flowfield and particle predictions. However, devolatilization rates are currently not well established, and this paper will not address this issue further.

The objectives of this paper are (1) to present theoretical results from an investigation of several thermal effects on devolatilization for single particles and in a comprehensive predictive model and (2) to illustrate the importance of considering chemistry/turbulence interactions when extending the model to allow for variable composition of the coal volatiles. The comprehensive model that was used is PCGC-2, Pulverized Coal Gasification or Combustion-2 Dimensional (axisymmetric). Thermal effects that were investigated include variable particle heat capacity, particle emissivity, heat of reaction during devolatilization, and volatiles heating value.

## Variable Particle Heat Capacity

Merrick (6) suggested the following function for coal heat capacity:

$$c_v = \left(\frac{R}{a}\right) \left[ g_1 \left( \frac{380}{T} \right) + 2g_1 \left( \frac{1800}{T} \right) \right] \quad 1)$$

where  $g_1$  is given by

$$g_1(z) = \frac{e^z}{\left[ \frac{(e^z - 1)}{z} \right]^2} \quad 2)$$

These equations can be used for both coal and char and predict a monotonic increase in  $c_v$  with temperature. However, because composition varies with time, the increase in  $c_v$  for a heating and reacting particle may not be monotonic due to changes in average atomic weight (6). The high temperature limit for Equation 1 is  $3R/a$ , which agrees with principles of physical chemistry.

Using Equation 1, Merrick obtained agreement between predicted and experimental values within about 10% over the temperature range of the available data (0-300°C) for various coal ranks (15-35% volatile matter). Graphite and char heat capacities were correlated within 5% over the range 0-800°C.

Calculations were carried out for single particles of 40 and 100 microns and for coal-water-slurry to test the effect of variable heat capacity on particle temperature and devolatilization rate. Particle heat capacities were calculated as the weighted sum of the heat capacities for raw coal, char, and ash. Gas temperature was assumed constant at 2100 K. Constant heat capacity cases were calculated using heat capacities calculated at 350 K and 525 K for the coal and char components, respectively. The two-equation model was used for devolatilization, with coefficients suggested by Ubhayakar et al. (Z). The average atomic weights for the coal and char were assumed to be 8.18 and 12.0, respectively, with the latter corresponding to pure carbon. The heat capacity of ash was taken to be (6)

$$c_v = 593.3 + 0.586 T$$

3)

The heat capacity of the particles at constant pressure was assumed equal to the heat capacity at constant volume. Radiative heat transfer and particle blowing were taken into account. However, oxidation was neglected to more clearly illustrate the effects of heat capacity.

Profiles of temperature and devolatilization rate for the 100-micron particles are shown in Figure 1. The gas temperature is also shown for comparison. Calculations for the 40-micron coal particles and coal-water slurry droplets showed similar effects of variable heat capacity during particle heatup. The initial heatup rate for the 100- $\mu$ m particles is approximately  $1.6 \times 10^5$  K/s for both constant and variable  $c_p$ . As particle temperature increases, heatup of the particle with variable  $c_p$  is retarded by the increasing value of  $c_p$ , as shown in Figure 1a, resulting in a temperature difference between the two particles of as much as 500 degrees K. This temperature lag results in a 50 percent increase in the time required for particle ignition and a slight decrease in the devolatilization rate, as shown in Figure 1b. The slower heatup rate during devolatilization allows a greater portion of the particle to devolatilize via the low-temperature reaction, thus giving an ultimate volatiles yield that is approximately 5 percent lower than for the particle with constant  $c_p$ .

As shown in Figure 1a, the heatup rate decreases markedly during devolatilization, due to the blowing effect. This effect was similarly predicted by Ubhayakar and coworkers (Z). The asymptotic temperature of both particles is approximately 200 degrees less than the gas temperature, due to radiative heat losses to the walls of the reactor, which were assumed to have a temperature of 1000 K.

Calculations were also performed with the comprehensive code (PCGC-2) for particles with constant and variable heat capacity. Contour plots of temperature for the constant and variable  $c_p$  cases are shown in Figures 2a and 2b, respectively. As shown, the temperature fields are similar, except that the temperature is somewhat lower in the variable  $c_p$  case. This can be seen by noting that the isotherms in Figure 2b are generally shifted toward the exit and centerline. The lower gas temperature was predominantly a result of the decrease in volatile yield from the coal. The delay in particle ignition caused by variable  $c_p$  is also apparent in Figure 2b on the centerline at the inlet.

The effect of variable heat capacity on total burnout is shown in Figure 3. The curve for variable  $c_p$  is shifted to the right, resulting in a decrease of approximately 3 percent in particle burnout at the exit of the reactor. This effect is consistent with the delayed ignition and slightly slower devolatilization rate observed in the single particle calculations. Interestingly, the decrease in burnout is approximately equal to the decrease in ultimate volatiles yield predicted for the single particles, even though particle oxidation was not ignored in the comprehensive predictions.

### Particle Emissivity

Total emissivities for coal particles have been reported with large variation, as summarized by Solomon et al. (8). Measurements by Brewster and Kunitomo (9) for micron-sized particles suggest that previous determinations of the imaginary part of the index of refraction for coal may be too high by an order of magnitude. If so, the calculated coal

emissivity for these particles based on previous values may also be too high. However, the experimental work of Baxter et al. (10) indicates that the effective emissivity of 100-micron coal particles of several ranks of coal at low temperatures is probably not less than 0.7.

To investigate the sensitivity of devolatilization to coal emissivity, calculations were again performed for single particles and with the comprehensive code. For the single particle cases, emissivity was varied between 0.9 and 0.1. In the comprehensive code calculations, emissivity was varied from 0.9 to 0.3. The wall temperature was 1250 K in the former and 1000 K in the latter.

Little effect of emissivity was noted in either set of calculations. The high gas temperature in the single particle calculations made convection/conduction the principal mode of heat transfer. In the comprehensive code simulations, the secondary air was swirled (swirl no. = 2), and the flow field was recirculating. Thus the particles were heated largely by contact with hot recirculating gases and not by radiation. In larger furnaces, or in reactors where the particles do not immediately contact hot gases, radiation may contribute significantly to particle heating, and in this case, greater sensitivity to the value of particle emissivity would be expected.

### Heat of Reaction

A similar investigation was initiated on the effect of heat of reaction for devolatilization. Investigators disagree on both the magnitude and sign of the heat of reaction. Reported values range from -65.3 kJ/kg to +334 KJ/kg (6,11). Merrick (6) speculates that the source of the disagreement is related to the effect of variable heat capacity. The heat of reaction probably varies with coal type. However, our preliminary conclusions are that devolatilization calculations are insensitive to this parameter, which agrees with the conclusion of Solomon and Serio (11). Investigation of the effect of heat of reaction is continuing.

### Volatiles Heating Value

The heating value of the coal volatiles must be known in order to calculate the energy released by gas-phase reactions. This heating value is a function of volatiles composition, which is a function of burnout. However, in comprehensive combustion simulations that treat the effects of chemistry/turbulence interactions (discussed in the next section), both heating value and composition of the volatiles are often assumed constant.

The effect of variable heating value was not tested in single particle calculations, because gas-phase reactions were not included in this model. The sensitivity of the comprehensive code to changing volatiles heating value was tested in an approximate manner by increasing the heat of formation of the coal. Since the volatiles enthalpy is calculated from a particle heat balance, and over 80 percent of the total particle mass loss was due to devolatilization, increasing the heat of formation of the coal effectively increased the volatiles heating value. A value was chosen such that the adiabatic flame temperature of the coal at a stoichiometric ratio of unity was increased by about 200 K. Since the simulations were performed for fuel-lean (combustion) conditions, the actual gas temperatures increased by 50-75 K.

The results of this investigation are shown in Figures 2 and 3. As shown in Figure 2c, the gas temperatures are seen to be higher with the increased heat of formation of coal. Otherwise the temperature fields are quite similar. The higher temperatures are due to a combination of higher heating value and greater volatiles yield. The latter effect dominates everywhere except in the near-burner region. The higher temperature significantly affects coal burnout, as shown in Figure 3, with a large portion of the impact coming from the volatile yield in the early regions of the reactor. The magnitude of the variation of the offgas heating value was arbitrary in this case, but is regarded as representative of actual coals and possibly conservative.

## Volatiles Composition

The variation of char and coal offgas composition with burnout has been correlated by both simple and complex reaction schemes (12-14). Accounting for this variation is not difficult for the particles. However, dealing with this variable composition and its interplay with gas phase turbulent mixing and kinetics is both complex and computationally expensive.

The successful prediction of turbulent and mean flow properties is a difficult proposition in typical combustion environments (15). Although reasonable success has been achieved for some simple flows, the complexity of reacting, swirling, turbulent flows often exceeds the capability of even sophisticated turbulence models. The added complexity of chemical effects on these predictions and the effect of turbulence on the mean reaction rates compounds the problem. Indeed, combustion investigators have identified this problem as one of the critical needs of combustion research (16).

Several approaches to the problem have been proposed. Some of these were recently reviewed and compared to data by Smith and Fletcher (17). The approach used in the current paper is the statistical, coal gas mixture fraction model. The detailed theory and assumptions of this model are given elsewhere (1). Only a brief discussion is given here.

The statistical, coal gas mixture fraction model involves convolving instantaneous properties over the turbulent statistics of the mixture to get time-mean properties. The statistics of the mixture is represented by the multivariate probability density function of a number of independent progress variables. The instantaneous mixture properties must all be represented as functions of only these progress variables.

The current code PCGC-2 allows for two progress variables. One progress variable is typically used for the inlet gas mixture fraction and the other is used for the coal offgas mixture fraction. The coal offgas composition is therefore assumed constant. Chemical kinetics are assumed fast for major gas species (intermixing of fuel and oxidizer is rate-limiting), so that the mixture is in local instantaneous equilibrium, and local properties depend only on the local elemental composition and enthalpy. With the two mixture fractions, the local composition is specified. Enthalpy fluctuations are assumed to be correlated with fluctuations in the stoichiometric ratio, as given by the two mixture fractions. Time-mean properties are therefore calculated by a double integral over the joint probability density function of the two mixture fractions. The evaluation of this integral consumes a significantly greater fraction of the computational time than any other single task in the code, even though a table of equilibrium properties is used to minimize the time spent performing equilibrium calculations.

Additional progress variables are required if coal offgas composition is to be allowed to vary. Each group of elements that are evolved from the coal must be tracked independently. Each additional progress variable for which the statistical variance is taken into account will increase the computational burden of this approach substantially. An investigation of the importance of variable coal offgas composition in a comprehensive code that treats chemistry/turbulence interactions has never been reported. Such an investigation would determine the extent to which such effects should be taken into account. It may be possible to ignore the turbulent fluctuations of some or all progress variables when allowing offgas composition to vary. If so, the computational burden would be reduced significantly.

The computational effort involved with the convolutions is not the only significant consideration in treating large numbers of progress variables. A multi-variate probability density function is required to perform the convolution. However, transport equations are typically written to describe individual probability density functions. To the extent that the fluctuations in the mixture fractions are independent of each other, the multi-variate pdf's will be equal to the product of the individual pdf's. However, as the number of progress variables increases, this independence will be difficult to maintain. Predicting the correlation coefficients will be difficult and the relevance of the model could be compromised.

A study of the impact of turbulent fluctuations on overall predictions was conducted to evaluate their importance. In this study, the fluctuations were either arbitrarily neglected or included, and the results of the comprehensive predictions under these assumptions were

compared. Similar results are shown by Smith and Fletcher (17). These results are an extension of their work, focusing on the effect of the coal offgas fluctuations. Figures 4, 5, and 6 show the results of ignoring turbulent fluctuations in the coal gas mixture fraction on gas temperature, total particle burnout, and centerline  $\text{NO}_x$  concentration. The coal gas mixture fraction  $\eta$  represents the degree of mixing between the coal volatiles and the inlet gas. As expected, neglecting the fluctuations in inlet gas mixture fraction had little effect on the calculations, since both the primary and secondary streams were air at 300 and 589 K, respectively.

The effect of ignoring the fluctuations in  $\eta$  on gas temperature can be seen by comparing Figures 2a and 4. Ignoring the fluctuations caused a high temperature ridge at the location of mixing between the primary and secondary streams, as can be seen by the higher concentration of isotherms in Figure 4. Taking the fluctuations into account smoothed the high temperature peaks. Similar observations were made by Smith and Fletcher (17) when they ignored turbulent fluctuations in both mixture fractions. Because the rate of mixing of fuel and oxidizer is reduced when turbulent fluctuations are ignored, the particle burnout is lowered as shown in Figure 5.

The above results were obtained assuming that the mixing is rate-limiting. The kinetics of  $\text{NO}_x$  formation and destruction are of the same order of magnitude as the turbulent mixing rates. Therefore, both mixing and kinetic considerations must be made to predict  $\text{NO}_x$  concentrations. The model used to do so has been previously reported (18) and incorporated as a submodel in PCGC-2.

Figure 6 shows the effect of the fluctuations on pollutant predictions. In Figure 6a, turbulent fluctuations were ignored both in the calculation of major species, and in the calculation of the pollutant species, which are decoupled from the calculation of major species. In Figure 6b, turbulent fluctuations were taken into account for both calculations. As shown, the predicted NO levels are quite sensitive to rigorous accounting for the effects of turbulence on chemistry. When turbulent fluctuations are taken into account, oxygen from the secondary mixes more rapidly with the primary, and more  $\text{NO}_x$  is formed. Although data were not available for comparison with this calculation, previously reported calculations have shown that solutions taking the turbulence into account agree more closely with data (18).

## Conclusions

Coal devolatilization is typically responsible for flame ignition and the ignition point and volatile yield of the devolatilization reactions have large impacts on overall combustion characteristics.

The temperature and composition dependence of particle heat capacity alters comprehensive code predictions of particle temperature, particle ignition, particle burnout, gas ignition and combustion efficiency. The effect is predominantly linked to the predicted ignition point of the coal and the extent of devolatilization.

For typical operating conditions of entrained-flow reactors (cold walls, hot gas), the value of coal particle emissivity does not significantly affect comprehensive code predictions. Preliminary results indicate that predictions are also insensitive to heat of devolatilization, but further investigation of this effect is needed. These conclusions may be different in situations with less dominant conductive/convective heat transfer.

The heating value of the coal offgas affects coal burnout and, to a lesser extent, gas temperature. This effect is attributed to the volatile yield of the coal under different heating conditions. Correlations of offgas heating value with particle burnout may improve comprehensive code predictions.

Turbulent fluctuations have an important impact on the mean reaction rate of coal offgas with the gas mixture. Further investigation of the importance of variable coal offgas composition in comprehensive codes and the importance of including the effect of turbulent fluctuations is proceeding.

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## List of Symbols

a	average atomic weight of coal or char (kg/kg-mol)
$c_v$	constant volume heat capacity (J/kg-K)
$g_1$	function defined by Equation 2
R	universal gas constant (8314.4 J/kg-mol/K)
T	temperature (K)
z	parameter in Equation 2

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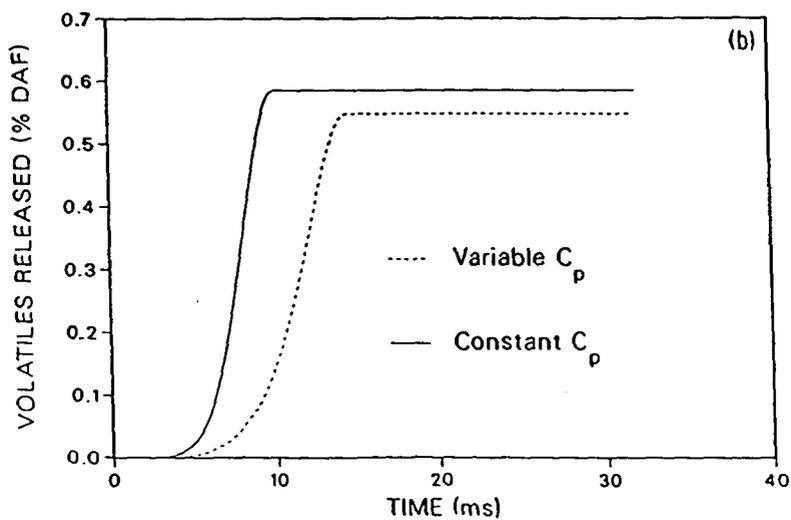
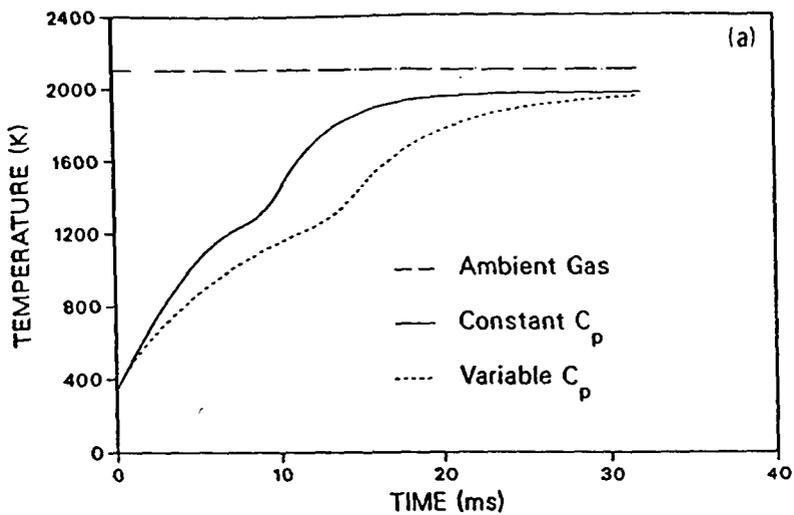


Figure 1. Variations of (a) particle temperature and (b) mass loss when different particle heat capacity formulations are used. The variable  $C_p$  case uses the correlation of Merrick (6).

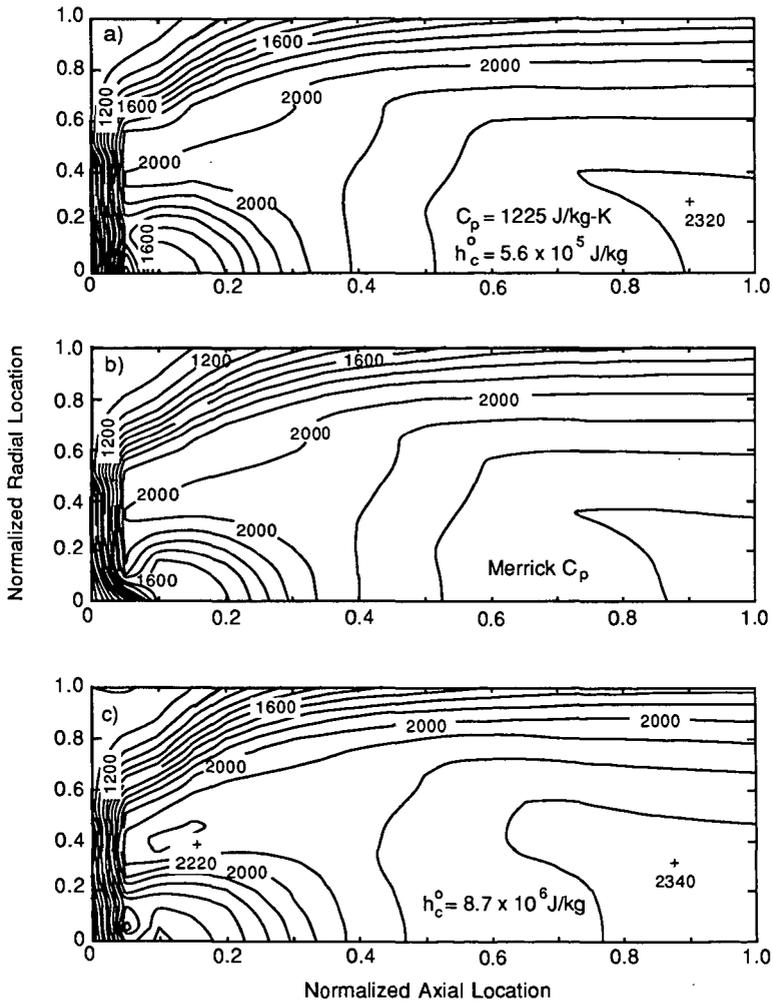


Figure 2. Contour plots of temperature for (a) constant particle heat capacity, (b) Merrick variable heat capacity, and (c) increased heat of formation of coal ( $h_c^\circ$ ).

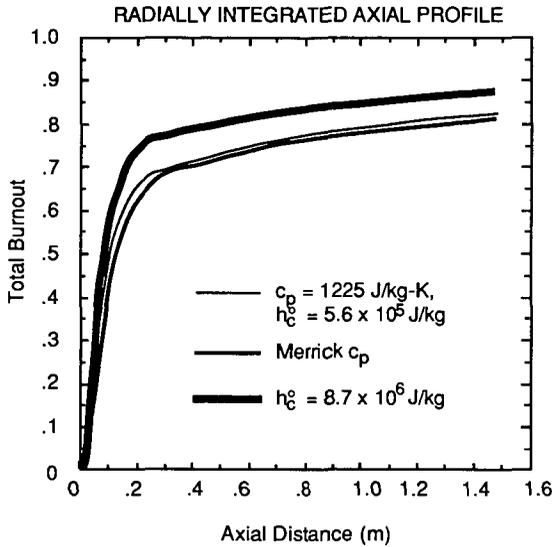


Figure 3. Effect of variable heat capacity and increased volatiles heating value on total particle burnout

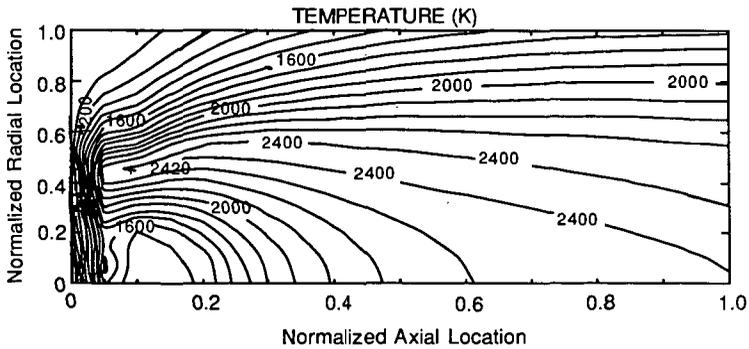


Figure 4. Gas temperature isotherms predicted when fluctuations in coal gas mixture fraction are neglected.

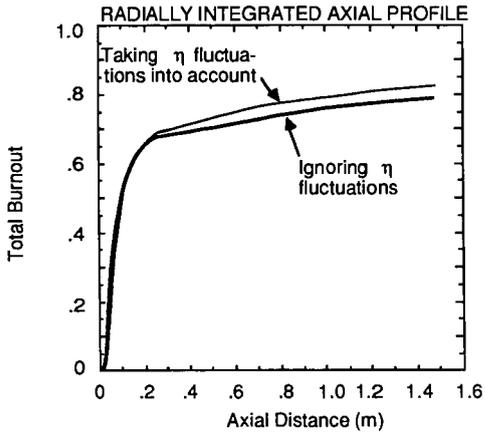


Figure 5. Effect of neglecting fluctuations in coal gas mixture fraction on total particle burnout.

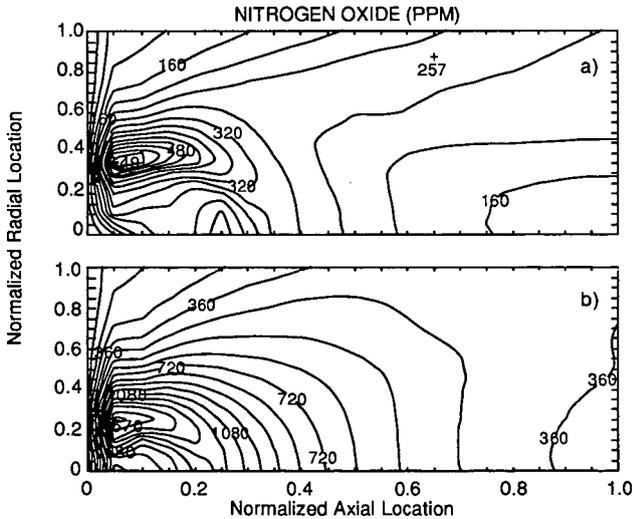


Figure 6. Predicted NO concentration (a) neglecting turbulent fluctuations of coal gas mixture fraction and (b) taking fluctuations into account.