Chapter 17. Modeling Pollutant Formation

This chapter discusses the models available in FLUENT for modeling pollutant formation.

Information is presented in the following sections:

- Section 17.1: NO\(_x\) Formation
- Section 17.2: Soot Formation

17.1 NO\(_x\) Formation

The following sections present the theoretical background of NO\(_x\) prediction and information about the usage of the NO\(_x\) models employed by the solver.

- Section 17.1.1: Overview and Limitations
- Section 17.1.2: Governing Equations for NO\(_x\) Transport
- Section 17.1.3: Thermal NO\(_x\) Formation
- Section 17.1.4: Prompt NO\(_x\) Formation
- Section 17.1.5: Fuel NO\(_x\) Formation
- Section 17.1.6: NO\(_x\) Formation by Reburning
- Section 17.1.7: NO\(_x\) Formation in Turbulent Flows
- Section 17.1.8: Using the NO\(_x\) Model
17.1.1 Overview and Limitations

NO\textsubscript{x} emission consists of mostly nitric oxide (NO). Less significant are nitrogen oxide (NO\textsubscript{2}) and nitrous oxide (N\textsubscript{2}O). NO\textsubscript{x} is a precursor for photochemical smog, contributes to acid rain, and causes ozone depletion. Thus, NO\textsubscript{x} is a pollutant. The FLUENT NO\textsubscript{x} model provides a tool to understand the sources of NO\textsubscript{x} production and to aid in the design of NO\textsubscript{x} control measures.

NO\textsubscript{x} Modeling in FLUENT

The FLUENT NO\textsubscript{x} model provides the capability to model thermal, prompt, and fuel NO\textsubscript{x} formation as well as NO\textsubscript{x} consumption due to reburning in combustion systems. It uses rate models developed at the Department of Fuel and Energy, The University of Leeds, England as well as from the open literature.

To predict NO\textsubscript{x} emission, FLUENT solves a transport equation for nitric oxide (NO) concentration. With fuel NO\textsubscript{x} sources, FLUENT solves an additional transport equation for an intermediate species (HCN or NH\textsubscript{3}). The NO\textsubscript{x} transport equations are solved based on a given flow field and combustion solution. In other words, NO\textsubscript{x} is postprocessed from a combustion simulation. It is thus evident that an accurate combustion solution becomes a prerequisite of NO\textsubscript{x} prediction. For example, thermal NO\textsubscript{x} production doubles for every 90 K temperature increase when the flame temperature is about 2200 K. Great care must be exercised to provide accurate thermophysical data and boundary condition inputs for the combustion model. Appropriate turbulence, chemistry, radiation and other submodels must be applied.

To be realistic, one can only expect results to be as accurate as the input data and the selected physical models. Under most circumstances, NO\textsubscript{x} variation trends can be accurately predicted but the NO\textsubscript{x} quantity itself cannot be pinpointed. Accurate prediction of NO\textsubscript{x} parametric trends can cut down on the number of laboratory tests, allow more design variations to be studied, shorten the design cycle, and reduce product development cost. That is truly the power of the FLUENT NO\textsubscript{x} model and, in fact, the power of CFD in general.
Implementing the Segregated Solver

The Formation of NO\textsubscript{x} in Flames

In laminar flames, and at the molecular level within turbulent flames, the formation of NO\textsubscript{x} can be attributed to four distinct chemical kinetic processes: thermal NO\textsubscript{x} formation, prompt NO\textsubscript{x} formation, fuel NO\textsubscript{x} formation, and reburning. Thermal NO\textsubscript{x} is formed by the oxidation of atmospheric nitrogen present in the combustion air. Prompt NO\textsubscript{x} is produced by high-speed reactions at the flame front, and fuel NO\textsubscript{x} is produced by oxidation of nitrogen contained in the fuel. The reburning mechanism reduces the total NO\textsubscript{x} formation by accounting for the reaction of NO with hydrocarbons. The FLUENT NO\textsubscript{x} model is able to simulate all four of these processes.

Restrictions on NO\textsubscript{x} Modeling

- You must use the segregated solver. The NO\textsubscript{x} models are not available with either of the coupled solvers.
- The NO\textsubscript{x} models cannot be used in conjunction with the premixed combustion model.

17.1.2 Governing Equations for NO\textsubscript{x} Transport

FLUENT solves the mass transport equation for the NO species, taking into account convection, diffusion, production and consumption of NO and related species. This approach is completely general, being derived from the fundamental principle of mass conservation. The effect of residence time in NO\textsubscript{x} mechanisms, a Lagrangian reference frame concept, is included through the convection terms in the governing equations written in the Eulerian reference frame. For thermal and prompt NO\textsubscript{x} mechanisms, only the NO species transport equation is needed:

\[
\frac{\partial}{\partial t}(\rho Y_{NO}) + \nabla \cdot (\rho \vec{v} Y_{NO}) = \nabla \cdot (\rho \vec{D} \nabla Y_{NO}) + S_{NO}
\]  \hspace{1cm} (17.1-1)

As discussed in Section 17.1.5, the fuel NO\textsubscript{x} mechanisms are more involved. The tracking of nitrogen-containing intermediate species is important. FLUENT solves a transport equation for the HCN or NH\textsubscript{3} species in addition to the NO species:
Modeling Pollutant Formation

\[
\frac{\partial}{\partial t}(\rho Y_{\text{HCN}}) + \nabla \cdot (\rho \vec{v} Y_{\text{HCN}}) = \nabla \cdot (\rho D Y_{\text{HCN}}) + S_{\text{HCN}} \tag{17.1-2}
\]

\[
\frac{\partial}{\partial t}(\rho Y_{\text{NH}_3}) + \nabla \cdot (\rho \vec{v} Y_{\text{NH}_3}) = \nabla \cdot (\rho D Y_{\text{NH}_3}) + S_{\text{NH}_3} \tag{17.1-3}
\]

where \(Y_{\text{HCN}}\), \(Y_{\text{NH}_3}\), and \(Y_{\text{NO}}\) are mass fractions of HCN, NH\(_3\), and NO in the gas phase. The source terms \(S_{\text{HCN}}\), \(S_{\text{NH}_3}\), and \(S_{\text{NO}}\) are to be determined next for different NO\(_x\) mechanisms.

### 17.1.3 Thermal NO\(_x\) Formation

The formation of thermal NO\(_x\) is determined by a set of highly temperature-dependent chemical reactions known as the extended Zeldovich mechanism. The principal reactions governing the formation of thermal NO\(_x\) from molecular nitrogen are as follows:

\[
\text{O} + \text{N}_2 \xrightarrow{k_{1.1}} \text{N} + \text{NO} \tag{17.1-4}
\]

\[
\text{N} + \text{O}_2 \xrightarrow{k_{1.2}} \text{O} + \text{NO} \tag{17.1-5}
\]

A third reaction has been shown to contribute, particularly at near-stoichiometric conditions and in fuel-rich mixtures:

\[
\text{N} + \text{OH} \xrightarrow{k_{1.3}} \text{H} + \text{NO} \tag{17.1-6}
\]

**Thermal NO\(_x\) Reaction Rates**

The rate constants for these reactions have been measured in numerous experimental studies [21, 70, 162], and the data obtained from these studies have been critically evaluated by Baulch et al. [11] and Hanson.
17.1 NO\textsubscript{x} Formation

and Salimian [88]. The expressions for the rate coefficients for Reactions 17.1-4–17.1-6 used in the NO\textsubscript{x} model are given below. These were selected based on the evaluation of Hanson and Salimian [88].

\begin{align*}
    k_1 &= 1.8 \times 10^8 e^{-38370/T} \text{ m}^3/\text{gmol-s} (17.1-7) \\
    k_{-1} &= 3.8 \times 10^7 e^{-425/T} \text{ m}^3/\text{gmol-s} (17.1-8) \\
    k_2 &= 1.8 \times 10^4 T e^{-4680/T} \text{ m}^3/\text{gmol-s} (17.1-9) \\
    k_{-2} &= 3.8 \times 10^3 T e^{-20820/T} \text{ m}^3/\text{gmol-s} (17.1-10) \\
    k_3 &= 7.1 \times 10^7 e^{-450/T} \text{ m}^3/\text{gmol-s} (17.1-11) \\
    k_{-3} &= 1.7 \times 10^8 e^{-24560/T} \text{ m}^3/\text{gmol-s} (17.1-12)
\end{align*}

In the above expressions, $k_1$, $k_2$, and $k_3$ are the rate constants for the forward reactions 17.1-4–17.1-6, respectively, and $k_{-1}$, $k_{-2}$, and $k_{-3}$ are the corresponding reverse rates.

The net rate of formation of NO via Reactions 17.1-4–17.1-6 is given by

\begin{align*}
    \frac{d[\text{NO}]}{dt} &= k_1[\text{O}][\text{N}_2] + k_2[\text{N}][\text{O}_2] + k_3[\text{N}][\text{OH}] - k_{-1}[\text{NO}][\text{N}] \\
    &\quad - k_{-2}[\text{NO}][\text{O}] - k_{-3}[\text{NO}][\text{H}] \quad (17.1-13)
\end{align*}

where all concentrations have units of gmol/m\textsuperscript{3}.

In order to calculate the formation rates of NO and N, the concentrations of O, H, and OH are required.
Modeling Pollutant Formation

The Quasi-Steady Assumption for [N]

The rate of formation of NO\textsubscript{x} is significant only at high temperatures (greater than 1800 K) because fixation of nitrogen requires the breaking of the strong N\textsubscript{2} triple bond (dissociation energy of 941 kJ/gmol). This effect is represented by the high activation energy of Reaction 17.1-4, which makes it the rate-limiting step of the extended Zeldovich mechanism. However, the activation energy for oxidation of N atoms is small. When there is sufficient oxygen, as in a fuel-lean flame, the rate of consumption of free nitrogen atoms becomes equal to the rate of its formation and therefore a quasi-steady state can be established. This assumption is valid for most combustion cases except in extremely fuel-rich combustion conditions. Hence the NO formation rate becomes

\[
\frac{d[\text{NO}]}{dt} = 2k_1[\text{O}][\text{N}_2] \left(1 - \frac{k_{-1}[\text{NO}^2]}{k_2[\text{O}_2]}\right) \left(1 + \frac{k_{-1}[\text{NO}]}{k_2[\text{O}_2]+k_3[\text{OH}]}\right) \text{ (gmol/m}^3\text{-s)} \quad (17.1-14)
\]

Sensitivity of Thermal NO\textsubscript{x} to Temperature

From Equation 17.1-14 it is clear that the rate of formation of NO will increase with increasing oxygen concentration. It also appears that thermal NO formation should be highly dependent on temperature but independent of fuel type. In fact, based on the limiting rate described in Equation 17.1-7, thermal NO\textsubscript{x} production rate doubles for every 90 K temperature increase beyond 2200 K.

Decoupling NO\textsubscript{x} and Flame Calculations

In order to solve Equation 17.1-14, concentration of O atoms and the free radical OH will be required in addition to concentration of stable species (i.e., O\textsubscript{2}, N\textsubscript{2}). Following the suggestion by Zeldovich, the thermal NO\textsubscript{x} formation mechanism can be decoupled from the main combustion process, by assuming equilibrium values of temperature, stable species, O atoms, and OH radicals. However, radical concentrations, O atoms in particular, are observed to be more abundant than their equilibrium levels. The effect of partial equilibrium O atoms on NO\textsubscript{x} formation rate
has been investigated [159] during laminar methane-air combustion. The results of these investigations indicate that the level of NO\textsubscript{X} emission can be underpredicted by as much as 28\% in the flame zone, when assuming equilibrium O-atom concentrations.

**Determining O Radical Concentration**

There has been little detailed study of radical concentration in industrial turbulent flames, but work [56] has demonstrated the existence of this phenomenon in turbulent diffusion flames. Presently, there is no definitive conclusion as to the effect of partial equilibrium on NO\textsubscript{X} formation rates in turbulent flames. Peters and Donnerhack [178] suggest that partial equilibrium radicals can account for no more than a 25\% increase in thermal NO\textsubscript{X} and that fluid dynamics has the dominant effect on NO\textsubscript{X} formation rate. Bilger et al. [18] suggest that in turbulent diffusion flames, the effect of O atom overshoot on NO\textsubscript{X} formation rate is very important.

In order to overcome this possible inaccuracy, one approach would be to couple the extended Zeldovich mechanism with a detailed hydrocarbon combustion mechanism involving many reactions, species, and steps. This approach has been used previously for research purposes [156]. However, long computer processing time has made the method economically unattractive and its extension to turbulent flows difficult.

To determine the O radical concentration, FLUENT uses one of three approaches—the equilibrium approach, the partial equilibrium approach, and the predicted concentration approach—in recognition of the ongoing controversy discussed above.

**Method 1: Equilibrium Approach**

The kinetics of the thermal NO\textsubscript{X} formation rate is much slower than the main hydrocarbon oxidation rate, and so most of the thermal NO\textsubscript{X} is formed after completion of combustion. Therefore, the thermal NO\textsubscript{X} formation process can often be decoupled from the main combustion reaction mechanism and the NO\textsubscript{X} formation rate can be calculated by assuming equilibration of the combustion reactions. Using this approach,
the calculation of the thermal NO$_x$ formation rate is considerably simplified. The assumption of equilibrium can be justified by a reduction in the importance of radical overshoots at higher flame temperature [55]. According to Westenberg [265], the equilibrium O-atom concentration can be obtained from the expression

$$[O] = k_p[O_2]^{1/2}$$  \hspace{1cm} (17.1-15)

With $k_p$ included, this expression becomes

$$[O] = 3.97 \times 10^5 T^{-1/2} [O_2]^{1/2} e^{-31090/T} \text{ gmol/m}^3$$  \hspace{1cm} (17.1-16)

where $T$ is in Kelvin.

**Method 2: Partial Equilibrium Approach**

An improvement to method 1 can be made by accounting for third-body reactions in the O$_2$ dissociation-recombination process:

$$O_2 + M \rightleftharpoons O + O + M$$  \hspace{1cm} (17.1-17)

Equation 17.1-16 is then replaced by the following expression [255]:

$$[O] = 36.64 T^{1/2} [O_2]^{1/2} e^{-27123/T} \text{ gmol/m}^3$$  \hspace{1cm} (17.1-18)

which generally leads to a higher partial O-atom concentration.

**Method 3: Predicted O Approach**

When the O-atom concentration is well-predicted using an advanced chemistry model (such as the flamelet submodel of the non-premixed model), $[O]$ can be taken simply from the local O-species mass fraction.
Determining OH Radical Concentration

FLUENT uses one of three approaches to determine the OH radical concentration: the exclusion of OH from the thermal NO\textsubscript{x} calculation approach, the partial equilibrium approach, and the use of the predicted OH concentration approach.

Method 1: Exclusion of OH Approach

In this approach, the third reaction in the extended Zeldovich mechanism (Equation 17.1-6) is assumed to be negligible through the following observation:

\[ k_2[O_2]_{eq} \gg k_3[OH]_{eq} \]

This assumption is justified for lean fuel conditions and is a reasonable assumption for most cases.

Method 2: Partial Equilibrium Approach

In this approach, the concentration of OH in the third reaction in the extended Zeldovich mechanism (Equation 17.1-6) is given by [12, 264]

\[ [OH] = 2.129 \times 10^2T^{-0.57}e^{-4595/T}[O]^{1/2}[H_2O]^{1/2} \text{gmol/m}^3 \quad (17.1-19) \]

Method 3: Predicted OH Approach

As in the predicted O approach, when the OH radical concentration is well-predicted using an advanced chemistry model such as the flamelet model, \([OH]\) can be taken directly from the local OH species mass fraction.

Summary

To summarize, thermal NO\textsubscript{x} formation rate is predicted by Equation 17.1-14. The O-atom concentration needed in Equation 17.1-14 is computed using Equation 17.1-16 for the equilibrium assumption, using
Equation 17.1-18 for a partial equilibrium assumption, or using the local O-species mass fraction. You will make the choice during problem setup. In terms of the transport equation for NO (Equation 17.1-1), the NO source term due to thermal NO$\textsubscript{X}$ mechanisms is

$$S_{\text{thermal,NO}} = M_{w,NO} \frac{d[NO]}{dt}$$  \hspace{1cm} \text{(17.1-20)}$$

where $M_{w,NO}$ is the molecular weight of NO, and $d[NO]/dt$ is computed from Equation 17.1-14.

### 17.1.4 Prompt NO$\textsubscript{X}$ Formation

It is known that during combustion of hydrocarbon fuels, the NO$\textsubscript{X}$ formation rate can exceed that produced from direct oxidation of nitrogen molecules (i.e., thermal NO$\textsubscript{X}$).

**Where and When Prompt NO$\textsubscript{X}$ Occurs**

The presence of a second mechanism leading to NO$\textsubscript{X}$ formation was first identified by Fenimore [63] and was termed “prompt NO$\textsubscript{X}$”. There is good evidence that prompt NO$\textsubscript{X}$ can be formed in a significant quantity in some combustion environments, such as in low-temperature, fuel-rich conditions and where residence times are short. Surface burners, staged combustion systems, and gas turbines can create such conditions [6].

At present the prompt NO$\textsubscript{X}$ contribution to total NO$\textsubscript{X}$ from stationary combustors is small. However, as NO$\textsubscript{X}$ emissions are reduced to very low levels by employing new strategies (burner design or furnace geometry modification), the relative importance of the prompt NO$\textsubscript{X}$ can be expected to increase.

**Prompt NO$\textsubscript{X}$ Mechanism**

Prompt NO$\textsubscript{X}$ is most prevalent in rich flames. The actual formation involves a complex series of reactions and many possible intermediate species. The route now accepted is as follows:
17.1 NO\textsubscript{x} Formation

\[ \text{CH} + \text{N}_2 \rightleftharpoons \text{HCN} + \text{N} \quad (17.1-21) \]

\[ \text{N} + \text{O}_2 \rightleftharpoons \text{NO} + \text{O} \quad (17.1-22) \]

\[ \text{HCN} + \text{OH} \rightleftharpoons \text{CN} + \text{H}_2\text{O} \quad (17.1-23) \]

\[ \text{CN} + \text{O}_2 \rightleftharpoons \text{NO} + \text{CO} \quad (17.1-24) \]

A number of species resulting from fuel fragmentation have been suggested as the source of prompt NO\textsubscript{x} in hydrocarbon flames (e.g., CH, CH\textsubscript{2}, C, C\textsubscript{2}H), but the major contribution is from CH (Equation 17.1-21) and CH\textsubscript{2}, via

\[ \text{CH}_2 + \text{N}_2 \rightleftharpoons \text{HCN} + \text{NH} \quad (17.1-25) \]

The products of these reactions could lead to formation of amines and cyano compounds that subsequently react to form NO by reactions similar to those occurring in oxidation of fuel nitrogen, for example:

\[ \text{HCN} + \text{N} \rightleftharpoons \text{N}_2 + \ldots. \quad (17.1-26) \]

**Factors of Prompt NO\textsubscript{x} Formation**

Prompt NO\textsubscript{x} formation is proportional to the number of carbon atoms present per unit volume and is independent of the parent hydrocarbon identity. The quantity of HCN formed increases with the concentration of hydrocarbon radicals, which in turn increases with equivalence ratio. As the equivalence ratio increases, prompt NO\textsubscript{x} production increases at first, then passes a peak, and finally decreases due to a deficiency in oxygen.
Primary Reaction

Reaction 17.1-21 is of primary importance. In recent studies [201], comparison of probability density distributions for the location of the peak NO\textsubscript{x} with those obtained for the peak CH have shown close correspondence, indicating that the majority of the NO\textsubscript{x} at the flame base is prompt NO\textsubscript{x} formed by the CH reaction. Assuming that Reaction 17.1-21 controls the prompt NO\textsubscript{x} formation rate,

\[
\frac{d[NO]}{dt} = k_0[CH][N_2] \quad (17.1-27)
\]

Modeling Strategy

There are, however, uncertainties about the rate data for the above reaction. From Reactions 17.1-21–17.1-25, it can be concluded that the prediction of prompt NO\textsubscript{x} formation within the flame requires coupling of the NO\textsubscript{x} kinetics to an actual hydrocarbon combustion mechanism. Hydrocarbon combustion mechanisms involve many steps and, as mentioned previously, are extremely complex and costly to compute. In the present NO\textsubscript{x} model, a global kinetic parameter derived by De Soete [223] is used. De Soete compared the experimental values of total NO\textsubscript{x} formation rate with the rate of formation calculated by numerical integration of the empirical overall reaction rates of NO\textsubscript{x} and N\textsubscript{2} formation. He showed that overall prompt formation rate can be predicted from the expression

\[
\frac{d[NO]}{dt} = (\text{overall prompt NO}_x \text{ formation rate}) - (\text{overall prompt N}_2 \text{ formation rate}) \quad (17.1-28)
\]

In the early stages of the flame, where prompt NO\textsubscript{x} is formed under fuel-rich conditions, the O concentration is high and the N radical almost exclusively forms NO\textsubscript{x} rather than nitrogen. Therefore, the prompt NO\textsubscript{x} formation rate will be approximately equal to the overall prompt NO\textsubscript{x} formation rate:
17.1 \( \text{NO}_x \) Formation

\[
\frac{d[\text{NO}]}{dt} = k_{pr}[\text{O}_2]^a[N_2][\text{FUEL}]e^{-E_a/RT} \tag{17.1-29}
\]

For \( \text{C}_2\text{H}_4 \) (ethylene)-air flames,

\[
k_{pr} = 1.2 \times 10^7 (RT/p)^{a+1}
\]

\[
E_a = 60 \text{ kcal/gmol}
\]

where \( a \) is the oxygen reaction order, \( R \) is the universal gas constant, and \( p \) is pressure (all in SI units). The rate of prompt \( \text{NO}_x \) formation is found to be of the first order with respect to nitrogen and fuel concentration, but the oxygen reaction order, \( a \), depends on experimental conditions.

**Rate for Most Hydrocarbon Fuels**

Equation 17.1-29 was tested against the experimental data obtained by Backmier et al. [4] for different mixture strengths and fuel types. The predicted results indicated that the model performance declined significantly under fuel-rich conditions and for higher hydrocarbon fuels. To reduce this error and predict the prompt \( \text{NO}_x \) adequately in all conditions, the De Soete model was modified using the available experimental data. A correction factor, \( f \), was developed, which incorporates the effect of fuel type, i.e., number of carbon atoms, and air-to-fuel ratio for gaseous aliphatic hydrocarbons. Equation 17.1-29 now becomes

\[
\frac{d[\text{NO}]}{dt} = f k_{pr}'[\text{O}_2]^a[N_2][\text{FUEL}]e^{-E_a'/RT} \tag{17.1-30}
\]

so that the source term due to prompt \( \text{NO}_x \) mechanism is

\[
S_{\text{prompt,NO}} = M_{w,\text{NO}} \frac{d[\text{NO}]}{dt} \tag{17.1-31}
\]

In the above equations,

\[
f = 4.75 + 0.0819 \; n - 23.2\phi + 32\phi^2 - 12.2\phi^3 \tag{17.1-32}
\]

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Modeling Pollutant Formation

\( n \) is the number of carbon atoms per molecule for the hydrocarbon fuel, and \( \phi \) is the equivalence ratio. The correction factor is a curve fit for experimental data, valid for aliphatic alkane hydrocarbon fuels \((C_nH_{2n+2})\) and for equivalence ratios between 0.6 and 1.6. For values outside the range, the appropriate limit should be used. Values of \( k'_{pr} \) and \( E'_a \) are selected in accordance with reference [58].

Here the concept of equivalence ratio refers to an overall equivalence ratio for the flame, rather than any spatially varying quantity in the flow domain. In complex geometries with multiple burners this may lead to some uncertainty in the specification of \( \phi \). However, since the contribution of prompt NO\(_x\) to the total NO\(_x\) emission is often very small, results are not likely to be biased significantly.

**Oxygen Reaction Order**

Oxygen reaction order depends on flame conditions. According to De Soete [223], oxygen reaction order is uniquely related to oxygen mole fraction in the flame:

\[
a = \begin{cases} 
1.0, & X_{O_2} \leq 4.1 \times 10^{-3} \\
-3.95 - 0.9 \ln X_{O_2}, & 4.1 \times 10^{-3} \leq X_{O_2} \leq 1.11 \times 10^{-2} \\
-0.35 - 0.1 \ln X_{O_2}, & 1.11 \times 10^{-2} < X_{O_2} < 0.03 \\
0, & X_{O_2} \geq 0.03
\end{cases}
\]

(17.1-33)

**17.1.5 Fuel NO\(_x\) Formation**

**Fuel-Bound N\(_2\)**

It is well known that nitrogen-containing organic compounds present in liquid or solid fossil fuel can contribute to the total NO\(_x\) formed during the combustion process. This fuel nitrogen is a particularly important source of nitrogen oxide emissions for residual fuel oil and coal, which typically contain 0.3–2% nitrogen by weight. Studies have shown that most of the nitrogen in heavy fuel oils is in the form of heterocycles and it is thought that the nitrogen components of coal are similar [107]. It
is believed that pyridine, quinoline, and amine type heterocyclic ring structures are of importance.

Reaction Pathways

The extent of conversion of fuel nitrogen to NO\textsubscript{x} is dependent on the local combustion characteristics and the initial concentration of nitrogen-bound compounds. Fuel-bound nitrogen-containing compounds are released into the gas phase when the fuel droplets or particles are heated during the devolatilization stage. From the thermal decomposition of these compounds, (aniline, pyridine, pyrroles, etc.) in the reaction zone, radicals such as HCN, NH\textsubscript{3}, N, CN, and NH can be formed and converted to NO\textsubscript{x}. The above free radicals (i.e., secondary intermediate nitrogen compounds) are subject to a double competitive reaction path. This chemical mechanism has been subject to several detailed investigations [157]. Although the route leading to fuel NO\textsubscript{x} formation and destruction is still not completely understood, different investigators seem to agree on a simplified model:

Recent investigations [94] have shown that hydrogen cyanide appears to be the principal product if fuel nitrogen is present in aromatic or cyclic form. However, when fuel nitrogen is present in the form of aliphatic amines, ammonia becomes the principal product of fuel nitrogen conversion.

In the FLUENT NO\textsubscript{x} model, sources of NO\textsubscript{x} emission for gaseous, liquid and coal fuels are considered separately. The nitrogen-containing intermediates are grouped to be HCN or NH\textsubscript{3} only. Two transport equations (17.1-1 and 17.1-2 or 17.1-3) are solved. The source terms $S_{\text{HCN}}$, $S_{\text{NH}_3}$, and $S_{\text{N}_2}$ are.
Modeling Pollutant Formation

$S_{\text{NH}_3}$, and $S_{\text{NO}}$ are to be determined next for different fuel types. Discussions to follow refer only to fuel NO$_x$ sources for $S_{\text{NO}}$. Contributions from thermal and prompt mechanisms have been discussed in previous sections.

**Fuel NO$_x$ from Gaseous and Liquid Fuels**

The fuel NO$_x$ mechanisms for gaseous and liquid fuels are based on different physics but the same chemical reaction pathways.

**Fuel NO$_x$ from Intermediate Hydrogen Cyanide (HCN)**

When HCN is used as the intermediate species:

\[ S_{\text{HCN}} = S_{\text{pl,HCN}} + S_{\text{HCN-1}} + S_{\text{HCN-2}} \]  (17.1-34)

\[ S_{\text{NO}} = S_{\text{NO-1}} + S_{\text{NO-2}} \]  (17.1-35)

HCN Production in a Gaseous Fuel

The rate of HCN production is equivalent to the rate of combustion of the fuel:

\[ S_{\text{pl,HCN}} = \frac{R_{c,\text{fuel}} Y_{\text{N,fuel}} M_{w,\text{HCN}}}{M_{w,N}} \]  (17.1-36)
17.1 NO\textsubscript{x} Formation

where \( S_{\text{pl, HCN}} \) = source of HCN (kg/m\(^3\)-s)

\( \mathcal{R}_{\text{ef}} \) = mean limiting reaction rate of fuel (kg/m\(^3\)-s)

\( Y_{N, \text{fuel}} \) = mass fraction of nitrogen in the fuel

The mean limiting reaction rate of fuel, \( \mathcal{R}_{\text{ef}} \), is calculated from the Magnussen combustion model, so the gaseous fuel NO\textsubscript{x} option is available only when the generalized finite-rate model is used.

HCN Production in a Liquid Fuel

The rate of HCN production is equivalent to the rate of fuel release into the gas phase through droplet evaporation:

\[
S_{\text{pl, HCN}} = \frac{S_{\text{fuel}} Y_{N, \text{fuel}} M_{w, HCN}}{M_{w, N} V}
\tag{17.1-37}
\]

where

- \( S_{\text{pl, HCN}} \) = source of HCN (kg/m\(^3\)-s)
- \( S_{\text{fuel}} \) = rate of fuel release from the liquid droplets to the gas (kg/s)
- \( Y_{N, \text{fuel}} \) = mass fraction of nitrogen in the fuel
- \( V \) = cell volume (m\(^3\))

HCN Consumption

The HCN depletion rates from reactions (1) and (2) in the above mechanism are the same for both gaseous and liquid fuels, and are given by De Soete [223] as

\[
\mathcal{R}_1 = A_1 X_{\text{HCN}} X_{O_2} e^{-E_1/RT}
\tag{17.1-38}
\]

\[
\mathcal{R}_2 = A_2 X_{\text{HCN}} X_{NO} e^{-E_2/RT}
\tag{17.1-39}
\]
Modeling Pollutant Formation

where \( R_1, R_2 \) = conversion rates of HCN (s\(^{-1}\))

\( T \) = instantaneous temperature (K)

\( X \) = mole fractions

\( A_1 \) = \( 3.5 \times 10^{10} \) s\(^{-1}\)

\( A_2 \) = \( 3.0 \times 10^{12} \) s\(^{-1}\)

\( E_1 \) = 67 kcal/gmol

\( E_2 \) = 60 kcal/gmol

The oxygen reaction order, \( a \), is calculated from Equation 17.1-33.

Since mole fraction is related to mass fraction through molecular weights of the species (\( M_{w,i} \)) and the mixture (\( M_{w,m} \)),

\[
X_i = Y_i \frac{M_{w,m}}{M_{w,i}} = Y_i \left( \frac{pRT}{P} \right) \quad (17.1-40)
\]

HCN Sources in the Transport Equation

The mass consumption rates of HCN which appear in Equation 17.1-34 are calculated as

\[
S_{HCN-1} = -R_1 \frac{M_{w,HCN}}{RT} \quad (17.1-41)
\]

\[
S_{HCN-2} = -R_2 \frac{M_{w,HCN}}{RT} \quad (17.1-42)
\]

where \( S_{HCN-1} \) = consumption rates of HCN in reactions 1 and 2 respectively (kg/m\(^3\)-s)

\( P \) = pressure (Pa)

\( T \) = mean temperature (K)

NO\(_x\) Sources in the Transport Equation

NO\(_x\) is produced in reaction 1 but destroyed in reaction 2. The sources for Equation 17.1-35 are the same for a gaseous as for a liquid fuel, and are evaluated as follows:
17.1 NO\textsubscript{x} Formation

\[
S_{\text{NO}^{-1}} = -S_{\text{HCN}^{-1}} \frac{M_{w,\text{NO}}}{M_{w,\text{HCN}}} = \mathcal{R}_1 \frac{M_{w,\text{NO}} p}{RT} \tag{17.1-43}
\]

\[
S_{\text{NO}^{-2}} = S_{\text{HCN}^{-2}} \frac{M_{w,\text{NO}}}{M_{w,\text{HCN}}} = -\mathcal{R}_2 \frac{M_{w,\text{NO}} p}{RT} \tag{17.1-44}
\]

**Fuel NO\textsubscript{x} from Intermediate Ammonia (NH\textsubscript{3})**

When NH\textsubscript{3} is used as the intermediate species:

\[
\text{Fuel Nitrogen} \rightarrow \text{NH}_3
\]

The source terms in the transport equations can be written as follows:

\[
S_{\text{NH}_3} = S_{\text{pl,NH}_3} + S_{\text{NH}_3^{-1}} + S_{\text{NH}_3^{-2}} \tag{17.1-45}
\]

\[
S_{\text{NO}} = S_{\text{NO}^{-1}} + S_{\text{NO}^{-2}} \tag{17.1-46}
\]

**NH\textsubscript{3} Production in a Gaseous Fuel**

The rate of NH\textsubscript{3} production is equivalent to the rate of combustion of the fuel:

\[
S_{\text{pl,NH}_3} = \mathcal{R}_{\text{cf}} Y_{\text{N, fuel}} \frac{M_{w,\text{NH}_3}}{M_{w,N}} \tag{17.1-47}
\]
Modeling Pollutant Formation

where

\[ S_{pl,NH_3} = \text{source of NH}_3 \ (kg/m^3 \cdot s) \]
\[ R_{cf} = \text{mean limiting reaction rate of fuel} \ (kg/m^3 \cdot s) \]
\[ Y_{N,fuel} = \text{mass fraction of nitrogen in the fuel} \]

The mean limiting reaction rate of fuel, \( R_{cf} \), is calculated from the Magnussen combustion model, so the gaseous fuel NO\(_x\) option is available only when the generalized finite-rate model is used.

NH\(_3\) Production in a Liquid Fuel

The rate of NH\(_3\) production is equivalent to the rate of fuel release into the gas phase through droplet evaporation:

\[ S_{pl,NH_3} = S_{fuel} Y_{N,fuel} \frac{M_{w,NH_3}}{M_{w,N}V} \quad (17.1-48) \]

where

\[ S_{pl,NH_3} = \text{source of NH}_3 \ (kg/m^3 \cdot s) \]
\[ S_{fuel} = \text{rate of fuel release from the liquid droplets to the gas} \ (kg/s) \]
\[ Y_{N,fuel} = \text{mass fraction of nitrogen in the fuel} \]
\[ V = \text{cell volume} \ (m^3) \]

NH\(_3\) Consumption

The NH\(_3\) depletion rates from reactions (1) and (2) in the above mechanism are the same for both gaseous and liquid fuels, and are given by De Soete [223] as

\[ R_1 = A_1 X_{NH_3} X_{O_2} e^{-E_1/RT} \quad (17.1-49) \]
\[ R_2 = A_2 X_{NH_3} X_{NO} e^{-E_2/RT} \quad (17.1-50) \]
17.1 NO\textsubscript{x} Formation

where \( R_1, R_2 \) = conversion rates of NH\textsubscript{3} (s\textsuperscript{-1})
\( T \) = instantaneous temperature (K)
\( X \) = mole fractions
\( A_1 \) = \( 4.0 \times 10^6 \) s\textsuperscript{-1}
\( A_2 \) = \( 1.8 \times 10^6 \) s\textsuperscript{-1}
\( E_1 \) = 133.9 kJ/gmol
\( E_2 \) = 113 kJ/gmol

The oxygen reaction order, \( a \), is calculated from Equation 17.1-33.

Since mole fraction is related to mass fraction through molecular weights of the species \((M_i)\) and the mixture \((M_m)\),

\[
X_i = Y_i \frac{M_{w,m}}{M_{w,i}} = \frac{Y_i}{M_{w,i}} \left( \frac{\rho RT}{p} \right) \tag{17.1-51}
\]

NH\textsubscript{3} Sources in the Transport Equation

The mass consumption rates of NH\textsubscript{3} which appear in Equation 17.1-45 are calculated as

\[
S_{NH_3-1} = -R_1 \frac{M_{w,NH_3} p}{RT} \tag{17.1-52}
\]

\[
S_{NH_3-2} = -R_2 \frac{M_{w,NH_3} p}{RT} \tag{17.1-53}
\]

where \( S_{NH_3-1} \) = consumption rates of NH\textsubscript{3} in reactions 1 and 2 respectively (kg/m\textsuperscript{3}-s)
\( p \) = pressure (Pa)
\( T \) = mean temperature (K)
\( R \) = universal gas constant

NO\textsubscript{x} Sources in the Transport Equation

NO\textsubscript{x} is produced in reaction 1 but destroyed in reaction 2. The sources for Equation 17.1-46 are the same for a gaseous as for a liquid fuel, and are evaluated as follows:
Modeling Pollutant Formation

\[ S_{NO-1} = -S_{NH_3-1} \frac{M_{w,NO}}{M_{w,NH_3}} = R_1 \frac{M_{w,NO} p}{RT} \]  (17.1-54)

\[ S_{NO-2} = S_{NH_3-2} \frac{M_{w,NO}}{M_{w,NH_3}} = -R_2 \frac{M_{w,NO} p}{RT} \]  (17.1-55)

Fuel NO\textsubscript{x} from Coal

Nitrogen in Char and in Volatiles

For the coal it is assumed that fuel nitrogen is distributed between the volatiles and the char. Since there is no reason to assume that \( N \) is equally distributed between the volatiles and the char, we have allowed the fraction of \( N \) in the volatiles and the char to be specified separately.

When HCN is used as the intermediate species, two variations of fuel NO\textsubscript{x} mechanisms for coal are included. When NH\textsubscript{3} is used as the intermediate species, two variations of fuel NO\textsubscript{x} mechanisms for coal are included, much like in the calculation of NO\textsubscript{x} production from the coal via HCN. It is assumed that fuel nitrogen is distributed between the volatiles and the char.

Coal Fuel NO\textsubscript{x} Scheme A [222]

The first HCN mechanism assumes that all char \( N \) converts to HCN which is then converted partially to NO [222]. The reaction pathway is described as follows:

```
Char N

Volatile N → HCN → NO → N\textsubscript{2}

1: O\textsubscript{2}  2: NO  3: Char

N\textsubscript{2}
```
With the first scheme, all char-bound nitrogen converts to HCN. Thus,

\[ S_{\text{char, HCN}} = \frac{S_c Y_{N,\text{char}} M_{w,\text{HCN}}}{M_{w,N} V} \]  

(17.1-56)

\[ S_{\text{char, NO}} = 0 \]  

(17.1-57)

where \( S_c \) = char burnout rate (kg/s)

\( Y_{N,\text{char}} \) = mass fraction of nitrogen in char

\( V \) = cell volume (m³)

**Coal Fuel NO\textsubscript{x} Scheme B [144]**

The second HCN mechanism assumes that all char N converts to NO directly [144]. The reaction pathway is described as follows:

According to Lockwood [144], the char nitrogen is released to the gas phase as NO directly, mainly as a desorption product from oxidized char nitrogen atoms. If this approach is followed, then

\[ S_{\text{char, HCN}} = 0 \]  

(17.1-58)

\[ S_{\text{char, NO}} = \frac{S_c Y_{N,\text{char}} M_{w,\text{NO}}}{M_{w,N} V} \]  

(17.1-59)
Modeling Pollutant Formation

Which HCN Scheme to Use?

The second HCN mechanism tends to produce more NO\textsubscript{x} emission than the first. In general, however, it is difficult to say which one outperforms the other.

The source terms for the transport equations are

\[ S_{\text{HCN}} = S_{\text{pvc,HCN}} + S_{\text{HCN}-1} + S_{\text{HCN}-2} \] (17.1-60)

\[ S_{\text{NO}} = S_{\text{char,NO}} + S_{\text{NO}-1} + S_{\text{NO}-2} + S_{\text{NO}-3} \] (17.1-61)

Source contributions \( S_{\text{HCN}-1}, S_{\text{HCN}-2}, S_{\text{NO}-1}, \) and \( S_{\text{NO}-2} \) are described previously. Therefore, only the heterogeneous reaction source, \( S_{\text{NO}-3} \), the char NO\textsubscript{x} source, \( S_{\text{char,NO}} \), and the HCN production source, \( S_{\text{pvc,HCN}} \), need to be considered.

\textit{NO\textsubscript{x} Reduction on Char Surface}

The heterogeneous reaction of NO reduction on the char surface has been modeled according to reference [134]:

\[ R_3 = A_3 e^{-E_3/kT} \bar{p}_{\text{NO}} \] (17.1-62)

where \( R_3 \) = rate of NO reduction (gmol/m\textsuperscript{2}BET-s)
\( \bar{p}_{\text{NO}} \) = mean NO partial pressure (atm)
\( E_3 \) = 34 kcal/gmol
\( A_3 \) = 230 gmol/m\textsuperscript{2}BET-s-atm
\( T \) = mean temperature (K)

The partial pressure \( \bar{p}_{\text{NO}} \) is calculated using Dalton's law:

\[ p_{\text{NO}} = X_{\text{NO}} p \]

The rate of NO consumption due to reaction 3 will then be
\[ S_{\text{NO}-3} = \frac{c_s A_{\text{BET}} M_{w,\text{NO}} R_3}{1000} \]

where \( A_{\text{BET}} \) = BET surface area (m\(^2\)/kg)
\( c_s \) = concentration of particles (kg/m\(^3\))
\( S_{\text{NO}-3} \) = NO consumption (kg/m\(^3\)-s)

BET Surface Area

The heterogeneous reaction involving char is mainly an adsorption process whose rate is directly proportional to the pore surface area. The pore surface area is also known as the BET surface area due to the researchers who pioneered the adsorption theory (Brunauer, Emmett and Teller [28]). For commercial adsorbents, the pore (BET) surface areas range from 100,000 to 2 million square meters per kilogram, depending on the microscopic structure. For coal, the BET area is typically 25,000 m\(^2\)/kg which is used as the default in FLUENT.

The overall source of HCN (\( S_{\text{pvc,HCN}} \)) is a combination of volatile contribution (\( S_{\text{vol,HCN}} \)) and char contribution (\( S_{\text{char,HCN}} \)):

\[ S_{\text{pvc,HCN}} = S_{\text{vol,HCN}} + S_{\text{char,HCN}} \]

HCN from Volatiles

The source of HCN from the volatiles is related to the rate of volatile release:

\[ S_{\text{vol,HCN}} = \frac{S_{\text{vol}} Y_{\text{N,vol}} M_{w,\text{HCN}}}{M_{w,N} V} \]

where
\( S_{\text{vol}} \) = source of volatiles originating from
the coal particles into the gas phase (kg/s)
\( Y_{\text{N,vol}} \) = mass fraction of nitrogen in the volatiles
\( V \) = cell volume (m\(^3\))

Calculation of sources related to char-bound nitrogen depends on the fuel NO\(_x\) scheme selection.
Modeling Pollutant Formation

Coal Fuel NO$_x$ Scheme C [222]

The first NH$_3$ mechanism assumes that all char N converts to NH$_3$ which is then converted partially to NO [222]. The reaction pathway is described as follows:

\[
\text{Char N} \rightarrow \text{Volatile N} \rightarrow \text{NH}_3 \rightarrow \text{NO} \rightarrow \text{N}_2
\]

In this scheme, all char-bound nitrogen converts to NH$_3$. Thus,

\[
S_{\text{char,NH}_3} = \frac{S_c Y_{N,\text{char}} M_{w,\text{NH}_3}}{M_{w,N} V} \quad (17.1-63)
\]

\[
S_{\text{char,NO}} = 0 \quad (17.1-64)
\]

where

- $S_c$ = char burnout rate (kg/s)
- $Y_{N,\text{char}}$ = mass fraction of nitrogen in char
- $V$ = cell volume ($m^3$)

Coal Fuel NO$_x$ Scheme D [144]

The second NH$_3$ mechanism assumes that all char N converts to NO directly [144]. The reaction pathway is described as follows:
According to Lockwood [144], the char nitrogen is released to the gas phase as NO directly, mainly as a desorption product from oxidized char nitrogen atoms. If this approach is followed, then

\[ S_{\text{char, NH}_3} = 0 \]  \hspace{1cm} (17.1-65)

\[ S_{\text{char, NO}} = \frac{S_Y N_{\text{char}} M_{w, NO}}{M_{w, N V}} \]  \hspace{1cm} (17.1-66)

**Which NH\textsubscript{3} Scheme to Use?**

The second NH\textsubscript{3} mechanism tends to produce more NO\textsubscript{x} emission than the first. In general, however, it is difficult to say which one outperforms the other.

The source terms for the transport equations are

\[ S_{\text{NH}_3} = S_{\text{pvc, NH}_3} + S_{\text{NH}_3-1} + S_{\text{NH}_3-2} \]  \hspace{1cm} (17.1-67)

\[ S_{\text{NO}} = S_{\text{char, NO}} + S_{\text{NO-1}} + S_{\text{NO-2}} + S_{\text{NO-3}} \]  \hspace{1cm} (17.1-68)

Source contributions \( S_{\text{NH}_3-1}, S_{\text{NH}_3-2}, S_{\text{NO-1}}, S_{\text{NO-2}}, S_{\text{NO-3}}, S_{\text{char, NO}} \) are described previously. Therefore, only the NH\textsubscript{3} production source, \( S_{\text{pvc, NH}_3} \), needs to be considered.
Modeling Pollutant Formation

The overall production source of NH$_3$ is a combination of volatile contribution ($S_{vol,NH_3}$), and char contribution ($S_{char,NH_3}$):

$$S_{pvc,NH_3} = S_{vol,NH_3} + S_{char,NH_3} \quad (17.1-69)$$

NH$_3$ from Volatiles

The source of NH$_3$ from the volatiles is related to the rate of volatile release:

$$S_{vol,NH_3} = \frac{S_{vol} Y_{N,vol} M_{w,NH_3}}{M_{w,N} V}$$

where

$S_{vol} =$ source of volatiles originating from the coal particles into the gas phase (kg/s)

$Y_{N,vol} =$ mass fraction of nitrogen in the volatiles

$V =$ cell volume ($m^3$)

Calculation of sources related to char-bound nitrogen depends on the fuel NO$_x$ scheme selection.

17.1.6 NO$_x$ Formation From Reburning

The reburning NO mechanism is a pathway whereby NO reacts with hydrocarbons and is subsequently reduced. In general:

$$CH_i + NO \rightarrow HCN + \text{products} \quad (17.1-70)$$

Three reburn reactions are modeled by FLUENT for 1600 $\leq T \leq 2100$:

$$CH + NO \overset{k_1}{\rightarrow} HCN + O \quad (17.1-71)$$

$$CH_2 + NO \overset{k_2}{\rightarrow} HCN + OH \quad (17.1-72)$$

$$CH_3 + NO \overset{k_3}{\rightarrow} HCN + H_2O \quad (17.1-73)$$
If the temperature is outside of this range, NO reburn will not be computed.

The rate constants for these reactions are taken from [23]:

\[
\begin{align*}
  k_1 &= 1 \times 10^8 \text{ m}^3/\text{gmol-s} \\
  k_2 &= 1.4 \times 10^6 e^{-550/T} \text{ m}^3/\text{gmol-s} \\
  k_3 &= 2 \times 10^5 \text{ m}^3/\text{gmol-s}
\end{align*}
\]

The NO depletion rate due to reburn is expressed as

\[
\frac{d[NO]}{dt} = -k_1[CH][NO] - k_2[CH_2][NO] - k_3[CH_3][NO]
\]

and the source term for the reburning mechanism in the NO transport equation can be calculated as

\[
S_{\text{reburning,NO}} = -M_w,NO \frac{d[NO]}{dt}
\]

To calculate the NO depletion rate due to reburning, FLUENT will obtain the concentrations of CH, CH$_2$, and CH$_3$ from the species mass fraction results of the combustion calculation. For this reason, you should include these species in the problem definition (either in prePDF—or in FLUENT).

### 17.1.7 NO$_x$ Formation in Turbulent Flows

The kinetic mechanisms of NO$_x$ formation and destruction described in the preceding sections have all been obtained from laboratory experiments using either a laminar premixed flame or shock-tube studies where molecular diffusion conditions are well defined. In any practical combustion system, however, the flow is highly turbulent. The turbulent mixing process results in temporal fluctuations in temperature and species concentration which will influence the characteristics of the flame.
The relationships among NO\textsubscript{x} formation rate, temperature, and species concentration are highly nonlinear. Hence, if time-averaged composition and temperature are employed in any model to predict the mean NO\textsubscript{x} formation rate, significant errors will result. Temperature and composition fluctuations must be taken into account by considering the probability density functions which describe the time variation.

**The Turbulence-Chemistry Interaction Model**

In turbulent combustion calculations, FLUENT solves the density-weighted time-averaged Navier-Stokes equations for temperature, velocity, and species concentrations or mean mixture fraction and variance. To calculate NO concentration, a time-averaged NO formation rate must be computed at each point in the domain using the averaged flow-field information.

Methods of modeling the mean turbulent reaction rate can be based on either moment methods [268] or probability density function (PDF) techniques [102]. FLUENT uses the PDF approach.

The PDF method described here applies to the NO\textsubscript{x} transport equations only. The preceding combustion simulation can use either the generalized finite rate chemistry model by Magnussen and Hjertager or the non-premixed combustion model. For details on these combustion models, please see Chapters 13 and 14.

**The PDF Approach**

The PDF method has proven very useful in the theoretical description of turbulent flow [103]. In the FLUENT NO\textsubscript{x} model, a single- or joint-variable PDF in terms of a normalized temperature, species mass fraction, or the combination of both is used to predict the NO\textsubscript{x} emission. If the non-premixed combustion model is used to model combustion, then a one- or two-variable PDF in terms of mixture fraction(s) is also available. The mean values of the independent variables needed for the PDF construction are obtained from the solution of the transport equations.
General Expression for Mean Reaction Rate

The mean turbulent reaction rate $\bar{w}$ can be described in terms of the instantaneous rate $w$ and a single or joint PDF of various variables. In general,

$$\bar{w} = \int \cdots \int w(V_1, V_2, \ldots) P(V_1, V_2, \ldots) dV_1 dV_2 \ldots \quad (17.1-79)$$

where $V_1, V_2, \ldots$ are temperature and/or the various species concentrations present. $P$ is the probability density function (PDF).

Mean Reaction Rate Used in FLUENT

The PDF is used for weighting against the instantaneous rates of production of NO (e.g., Equation 17.1-20) and subsequent integration over suitable ranges to obtain the mean turbulent reaction rate. Hence we have

$$\overline{S}_{NO} = \int S_{NO}(V_1) P_1(V_1) dV_1 \quad (17.1-80)$$

or, for two variables

$$\overline{S}_{NO} = \int \int S_{NO}(V_1, V_2) P(V_1, V_2) dV_1 dV_2 \quad (17.1-81)$$

where $\overline{S}_{NO}$ is the mean turbulent rate of production of NO, $S_{NO}$ is the instantaneous rate of production given by, for example, Equation 17.1-20, and $P_1(V_1)$ and $P(V_1, V_2)$ are the PDFs of the variables $V_1$ and, if relevant, $V_2$. The same treatment applies for the HCN or NH$_3$ source terms.

Equation 17.1-80 or 17.1-81 must be integrated at every node and at every iteration. For a PDF in temperature, the limits of integration are determined from the minimum and maximum values of temperature in the combustion solution. For a PDF in mixture fraction, the limits of the integrations in Equation 17.1-80 or 17.1-81 are determined from the values stored in the look-up tables.
Modeling Pollutant Formation

Statistical Independence

In the case of the two-variable PDF, it is further assumed that the variables \( V_1 \) and \( V_2 \) are statistically independent so that \( P(V_1, V_2) \) can be expressed as

\[
P(V_1, V_2) = P_1(V_1)P_2(V_2)
\]

Beta PDF Assumed

\( P \) is assumed to be a two-moment beta function as appropriate for combustion calculations [87, 158]. The equation for the beta function is

\[
P(V) = \frac{\Gamma(\alpha + \beta)}{\Gamma(\alpha)\Gamma(\beta)}V^{\alpha-1}(1-V)^{\beta-1} = \frac{V^{\alpha-1}(1-V)^{\beta-1}}{\int_0^1 V^{\alpha-1}(1-V)^{\beta-1}dV}
\]

where \( \Gamma( ) \) is the Gamma function, \( \alpha \) and \( \beta \) depend on \( \bar{m} \), the mean value of the quantity in question, and its variance, \( \sigma^2 \):

\[
\alpha = \bar{m}\left(\frac{\bar{m}(1-\bar{m})}{\sigma^2} - 1\right)
\]

\[
\beta = (1-\bar{m})\left(\frac{\bar{m}(1-\bar{m})}{\sigma^2} - 1\right)
\]

The beta function requires that the independent variable \( V \) assume values between 0 and 1. Thus, field variables such as temperature must be normalized.

Calculation Method for \( \sigma^2 \)

The variance, \( \sigma^2 \), can be computed by solving a transport equation during the combustion calculation stage. This approach is compute-intensive and is not applicable for a postprocessing treatment of NO\(_x\)
prediction. Instead, calculation of \( \sigma^2 \) is based on an approximate form of the variance transport equation.

A transport equation for the variance \( \sigma^2 \) can be derived:

\[
\frac{\partial}{\partial t} \left( \rho \sigma^2 \right) + \nabla \cdot (\rho \overline{v} \sigma^2) = \nabla \left( \frac{\mu_t}{\sigma_t} \nabla \sigma^2 \right) + C_g \mu_t (\nabla \overline{m})^2 - C_d \rho \frac{\varepsilon}{k} \sigma^2 \tag{17.1-86}
\]

where the constants \( \sigma_t, C_g \) and \( C_d \) take the values 0.85, 2.86, and 2.0, respectively. Assuming equal production and dissipation of variance, one gets

\[
\sigma^2 = \frac{\mu_t k}{\rho \varepsilon} \frac{C_g}{C_d} (\nabla \overline{m})^2 = \frac{\mu_t k}{\rho \varepsilon} \frac{C_g}{C_d} \left[ \left( \frac{\partial \overline{m}}{\partial x} \right)^2 + \left( \frac{\partial \overline{m}}{\partial y} \right)^2 + \left( \frac{\partial \overline{m}}{\partial z} \right)^2 \right] \tag{17.1-87}
\]

The term in the brackets is the dissipation rate of the independent variable.

For a PDF in mixture fraction, the mixture fraction variance has already been solved as part of the basic combustion calculation, so no additional calculation for \( \sigma^2 \) is required.

### 17.1.8 Using the NO\(_x\) Model

**Decoupled Analysis: Overview**

NO\(_x\) concentrations generated in combustion systems are generally low. As a result, NO\(_x\) chemistry has negligible influence on the predicted flow field, temperature, and major combustion product concentrations. It follows that the most efficient way to use the NO\(_x\) model is as a postprocessor to the main combustion calculation.

The recommended procedure is as follows:

1. Calculate your combustion problem using FLUENT as usual.
2. Activate the desired NO\textsubscript{x} models (thermal, fuel, and/or prompt NO\textsubscript{x}, with or without reburn) and set the appropriate parameters, as described in this section.

3. In the Solution Controls panel, turn off solution of all variables except species NO and, if the fuel NO\textsubscript{x} submodel is activated, HCN or NH\textsubscript{3}.

4. Also in the Solution Controls panel, set a suitable value for the NO (and HCN or NH\textsubscript{3}, if appropriate) under-relaxation. A value of 0.8 to 1.0 is suggested, although lower values may be required for certain problems. That is, if convergence cannot be obtained, try a lower under-relaxation value.

5. In the Residual Monitors panel, decrease the convergence criterion for NO (and HCN or NH\textsubscript{3}, if appropriate) to 10^{-6}.

6. Perform calculations until convergence (i.e., until the NO (and HCN or NH\textsubscript{3}, if solved) species residuals are below 10^{-6}) to ensure that the NO and HCN or NH\textsubscript{3} concentration fields are no longer evolving.

7. Review the mass fractions of NO (and HCN or NH\textsubscript{3}) with alphanumeric and/or graphics tools in the usual way.

8. Save a new set of case and data files, if desired.

Inputs specific to the calculation of NO\textsubscript{x} formation are explained in the remainder of this section.

**Activating the NO\textsubscript{x} Models**

To activate the NO\textsubscript{x} models and set related parameters, you will use the NOx Model panel (Figure 17.1.1).
17.1 NO\textsubscript{x} Formation

Figure 17.1.1: The NO\textsubscript{x} Model Panel
Modeling Pollutant Formation

Under Models, select the NO\textsubscript{x} models to be used in the calculation of the NO and HCN concentrations:

- To enable thermal NO\textsubscript{x}, turn on the Thermal NO option.
- To enable prompt NO\textsubscript{x}, turn on the Prompt NO option.
- To enable fuel NO\textsubscript{x}, turn on the Fuel NO option.
- To enable NO reburn, turn on the Reburn option. (Note that the Reburn option will not appear until you have activated one of the other NO models listed above.)

Your selection(s) for Models will activate the calculation of thermal, prompt, and/or fuel NO, with or without reburn, in accordance with the chemical kinetic models described in Sections 17.1.3–17.1.6. Mean NO formation rates will be computed directly from mean concentrations and temperature in the flow field.

Setting Thermal NO\textsubscript{x} Parameters

The NO\textsubscript{x} routines employ three methods for calculation of thermal NO\textsubscript{x} (as described in Section 17.1.3). You will specify the method to be used in the NOx Model panel, under Thermal NO Parameters:

- To choose the equilibrium method, select Equilibrium in the [O] Model drop-down list.
- To choose the partial equilibrium method, select Partial-equilibrium in the [O] Model or [OH] Model drop-down list.
- To use the predicted O and/or OH concentration, select Instantaneous in the [O] Model or [OH] Model drop-down list.

Setting Prompt NO\textsubscript{x} Parameters

Prompt NO formation is predicted using Equations 17.1-30 and 17.1-32. The parameters are entered under Prompt NO Parameters in the NOx Model panel:
• Specify which of the defined species is the fuel by choosing it in the Fuel Species drop-down list.

• Set the Fuel Carbon Number (number of carbon atoms per fuel molecule)

• Set the Equivalence Ratio:

\[
\text{Equivalence Ratio} = \frac{\text{actual air-to-fuel ratio}}{\text{stoichiometric air-to-fuel ratio}}
\]

**Setting Fuel NO\textsubscript{x} Parameters**

For fuel NO\textsubscript{x} models, you will first need to specify the fuel type under Fuel NO Parameters:

• For gaseous fuel NO\textsubscript{x}, select Gas under Fuel Type.

• For liquid fuel NO\textsubscript{x}, select Liquid under Fuel Type.

• For solid fuel NO\textsubscript{x}, select Solid under Fuel Type.

Note that you can use only one of the fuel models at a time.

**Setting Gaseous and Liquid Fuel NO\textsubscript{x} Parameters**

If you have selected Gas or Liquid as the Fuel Type under Fuel NO Parameters, you will also need to specify the following:

• Select the intermediate species (HCN or NH\textsubscript{3}) in the N Intermediate drop-down list.

• Set the correct mass fraction of nitrogen in the fuel (kg nitrogen per kg fuel) in the Fuel N Mass Fraction field

**FLUENT** will use Equations 17.1-34 and 17.1-35 (for HCN) or Equations 17.1-45 and 17.1-46 (for NH\textsubscript{3}) to predict NO formation for a gaseous or liquid fuel.
Modeling Pollutant Formation

Setting Solid (Coal) Fuel NO\textsubscript{x} Parameters

For solid fuel, FLUENT will use Equations 17.1-60 and 17.1-61 (for HCN) or Equations 17.1-67 and 17.1-68 (for NH\textsubscript{3}) to predict NO formation. Several inputs (under Fuel NO Parameters) are required for the coal fuel NO\textsubscript{x} model:

- Select the intermediate species (HCN or NH\textsubscript{3}) in the N Intermediate drop-down list.
- Specify the mass fraction of nitrogen in the volatiles and in the char in the Volatile N Mass Fraction and Char N Mass Fraction fields, respectively.
- Define the BET internal pore surface area (see Section 17.1.5 for details) of the particles in the BET Surface Area field.
- Select the char N conversion path from the Char N Conversion drop-down list as NO\textsubscript{x}, HCN, or NH\textsubscript{3}. Note that HCN or NH\textsubscript{3} can be selected only if the same species has been selected as the intermediate species in the N Intermediate drop-down list.

Setting Parameters for NO\textsubscript{x} Reburn

There are no special parameters to specify for the NO\textsubscript{x} reburn model. When you use this model, however, you must be sure to include the species CH, CH\textsubscript{2}, and CH\textsubscript{3} in your problem definition, as warned in the Reburn Parameters section of the NOx Model panel. See Section 17.1.6 for details.

Setting Turbulence Parameters

If you want to take into account turbulent fluctuations (as described in Section 17.1.7) when you compute the specified NO formation (thermal, prompt, and/or fuel, with or without reburn), select one of the options in the PDF Mode drop-down list under Turbulence Interaction.

- Select Temperature to take into account fluctuations of temperature.
• Select Temperature/Species to take into account fluctuations of temperature and mass fraction of the species selected in the Species drop-down list (which appears when you select this option).

• Select Species_1/Species_2 to take into account the fluctuation of mass fractions of two species selected in the Species 1 and Species 2 drop-down lists (which appear when you select this option).

• (non-premixed combustion calculations only) Select Mixture Fraction to take into account fluctuation in the mixture fraction(s).

The Mixture Fraction option is available only if you are using the non-premixed combustion model to model the reacting system. If the Mixture Fraction option is used, the instantaneous temperatures, density, and species concentrations are taken from the PDF look-up table (created by prePDF) as a function of mixture fraction. The beta PDF in mixture fraction is calculated from the values of mean mixture fraction and variance at each cell. After the instantaneous NO\(_x\) rates have been calculated at each cell, they are convoluted with the mixture fraction PDF to yield the mean rates in turbulent flow.

Extra Input for Non-Adiabatic Non-Premixed Combustion Calculations Using a PDF in Mixture Fraction

If you choose the Mixture Fraction option and you are using the non-adiabatic non-premixed combustion model, an additional option (Use Top Temperature) will appear under Turbulence Interaction. When this option is off (the default condition) the local cell enthalpy is used to calculate the instantaneous temperature used in the NO\(_x\) rate calculation. This option should be used in most cases. If you enable Use Top Temperature, then in the part of the domain where the turbulent fluctuations are significant, the instantaneous temperatures are calculated in terms of the lowest heat loss (or highest heat gain) in that part of the domain. (In the equations in Section 14.1.2, the heat loss/gain is \(H^*\).) The result of this calculation will be the maximum possible NO\(_x\) production that can be calculated through the convolution with the mixture fraction PDF. By comparing the default results with those generated using the top temperature option, you can determine how sensitive the NO\(_x\)
Modeling Pollutant Formation

calculation is to the local enthalpy variation when the fluctuations are significant.

Number of Beta Points

You can, optionally, adjust the number of Beta PDF Points. The default value of 10, indicating that the beta function in Equation 17.1-80 or Equation 17.1-81 will be integrated at 10 points on a histogram basis, will yield an accurate solution with reasonable computation time. Increasing this value may improve accuracy, but will also increase the computation time.

Specifying a User-Defined Function for the NO\textsubscript{x} Rate

You can, optionally, choose to specify a user-defined function for the rate of NO\textsubscript{x} production. The rate returned from the UDF is added to the rate returned from the standard NO\textsubscript{x} production options, if any are selected. You can also choose to deselect all of the standard NO\textsubscript{x} production options and use only the UDF rate.

Select the desired function in the NO\textsubscript{x} Rate drop-down list under User-Defined Functions. See the separate UDF Manual for details about user-defined functions.

Postprocessing

When you compute NO\textsubscript{x} formation, the following additional variables will be available for postprocessing:

- Mass fraction of NO
- Mass fraction of HCN (appropriate fuel NO\textsubscript{x} model only)
- Mass fraction of NH\textsubscript{3} (appropriate fuel NO\textsubscript{x} model only)
- Mole fraction of NO
- Mole fraction of HCN (appropriate fuel NO\textsubscript{x} model only)
- Mole fraction of NH\textsubscript{3} (appropriate fuel NO\textsubscript{x} model only)
17.2 Soot Formation

- Concentration of NO
- Concentration of HCN (appropriate fuel NO\textsubscript{x} model only)
- Concentration of NH\textsubscript{3} (appropriate fuel NO\textsubscript{x} model only)
- Variance of Temperature (variance of normalized temperature)

These variables are contained in the NO\textsubscript{x}... category of the variable selection drop-down list that appears in postprocessing panels.

17.2 Soot Formation

Information about soot formation is presented in the following sections:

- Section 17.2.1: Overview and Limitations
- Section 17.2.2: Theory
- Section 17.2.3: Using the Soot Models

17.2.1 Overview and Limitations

FLUENT provides two empirical models for the prediction of soot formation in combustion systems. In addition, the predicted soot concentration can be included in the prediction of radiation absorption coefficients within the combustion system. You can include the effect of soot on radiation absorption when you use the P-1, discrete ordinates, or discrete transfer radiation model with a variable absorption coefficient.

Predicting Soot Formation

FLUENT predicts soot concentrations in a combustion system using one of two available models:

- the single-step Khan and Greeves model [113], in which FLUENT predicts the rate of soot formation based on a simple empirical rate.
Modeling Pollutant Formation

- the two-step Tesner model [149, 242], in which FLUENT predicts the formation of nuclei particles, with soot formation on the nuclei.

The Khan and Greeves model is the default model used by FLUENT when you include soot formation. In both models, combustion of the soot (and particle nuclei) is assumed to be governed by the Magnussen combustion rate [149]. Note that this limits the use of the soot formation models to turbulent flows. Soot formation cannot be predicted by FLUENT for laminar or inviscid flows.

Both soot formation models are empirically-based, approximate models of the soot formation process in combustion systems. The detailed chemistry and physics of soot formation are quite complex and are only approximated in the models used by FLUENT. You should view the results of these models as qualitative indicators of your system performance unless you can undertake experimental validation of the results.

Restrictions on Soot Modeling

The following restrictions apply to soot formation models:

- You must use the segregated solver. The soot models are not available with either of the coupled solvers.
- Soot formation can be modeled only for turbulent flows.
- The soot model cannot be used in conjunction with the premixed combustion model.

17.2.2 Theory

The Single-Step Soot Formation Model

In the single-step Khan and Greeves model [113], FLUENT solves a single transport equation for the soot mass fraction:

\[
\frac{\partial}{\partial t}(\rho Y_{\text{soot}}) + \nabla \cdot (\rho \vec{v} Y_{\text{soot}}) = \nabla \cdot \left( \frac{\mu_t}{\sigma_{\text{soot}}} \nabla Y_{\text{soot}} \right) + R_{\text{soot}} \quad (17.2-1)
\]
17.2 Soot Formation

where

\( Y_{\text{soot}} \) = soot mass fraction

\( \sigma_{\text{soot}} \) = turbulent Prandtl number for soot transport

\( R_{\text{soot}} \) = net rate of soot generation (kg/m\(^3\)-s)

\( R_{\text{soot}} \), the net rate of soot generation, is the balance of soot formation, \( R_{\text{soot, form}} \), and soot combustion, \( R_{\text{soot, comb}} \):

\[
R_{\text{soot}} = R_{\text{soot, form}} - R_{\text{soot, comb}} \quad (17.2-2)
\]

The rate of soot formation is given by a simple empirical rate expression:

\[
R_{\text{soot, form}} = C_s p_{\text{fuel}} \phi^r e^{-E/RT} \quad (17.2-3)
\]

where

\( C_s \) = soot formation constant (kg/N-m-s)

\( p_{\text{fuel}} \) = fuel partial pressure (Pa)

\( \phi \) = equivalence ratio

\( r \) = equivalence ratio exponent

\( E/RT \) = activation temperature (K)

The rate of soot combustion is the minimum of two rate expressions [149]:

\[
R_{\text{soot, comb}} = \min[ R_1, R_2 ] \quad (17.2-4)
\]

The two rates are computed as

\[
R_1 = A \rho Y_{\text{soot}} \frac{\epsilon}{k} \quad (17.2-5)
\]

and

\[
R_2 = A \rho \left( \frac{Y_{\text{ox}}}{\nu_{\text{soot}}} \right) \left( \frac{Y_{\text{soot}} \nu_{\text{soot}}}{Y_{\text{soot}} \nu_{\text{soot}} + Y_{\text{fuel}} \nu_{\text{fuel}}} \right) \frac{\epsilon}{k} \quad (17.2-6)
\]
Modeling Pollutant Formation

where
\[ A = \text{constant in the Magnussen model} \]
\[ Y_{\text{ox}}, Y_{\text{fuel}} = \text{mass fractions of oxidizer and fuel} \]
\[ \nu_{\text{soot}}, \nu_{\text{fuel}} = \text{mass stoichiometries for soot and fuel combustion} \]

The default constants for the single-step model are valid for a wide range of hydrocarbon fuels.

The Two-Step Soot Formation Model

The two-step Tesner model [242] predicts the generation of radical nuclei and then computes the formation of soot on these nuclei. FLUENT thus solves transport equations for two scalar quantities: the soot mass fraction (Equation 17.2-1) and the normalized radical nuclei concentration:

\[
\frac{\partial}{\partial t} (\rho b_{\text{nuc}}^*) + \nabla \cdot (\rho \vec{v} b_{\text{nuc}}^*) = \nabla \cdot \left( \frac{\mu}{\sigma_{\text{nuc}}} \nabla b_{\text{nuc}}^* \right) + R_{\text{nuc}}^* \tag{17.2-7}
\]

where
\[ b_{\text{nuc}}^* = \text{normalized radical nuclei concentration} \]
\[ (\text{particles } \times 10^{-15}/\text{kg}) \]
\[ \sigma_{\text{nuc}} = \text{turbulent Prandtl number for nuclei transport} \]
\[ R_{\text{nuc}}^* = \text{normalized net rate of nuclei generation} \]
\[ (\text{particles } \times 10^{-15}/\text{m}^3\text{-s}) \]

In these transport equations, the rates of nuclei and soot generation are the net rates, involving a balance between formation and combustion.

Soot Generation Rate

The two-step model computes the net rate of soot generation, \( R_{\text{soot}} \), in the same way as the single-step model, as a balance of soot formation and soot combustion:

\[
R_{\text{soot}} = R_{\text{soot,form}} - R_{\text{soot,comb}} \tag{17.2-8}
\]

In the two-step model, however, the rate of soot formation, \( R_{\text{soot,form}} \), depends on the concentration of radical nuclei, \( c_{\text{nuc}} \):
17.2 Soot Formation

\[ \mathcal{R}_{\text{soot,form}} = m_p (\alpha - \beta N_{\text{soot}}) c_{\text{nuc}} \]  \hspace{1cm} (17.2-9)

where

- \( m_p \) = mean mass of soot particle (kg/particle)
- \( N_{\text{soot}} \) = concentration of soot particles (particles/m^3)
- \( c_{\text{nuc}} \) = radical nuclei concentration = \( p_{\text{nuc}} \) (particles/m^3)
- \( \alpha \) = empirical constant (s^{-1})
- \( \beta \) = empirical constant (m^3/particle-s)

The rate of soot combustion, \( \mathcal{R}_{\text{soot,comb}} \), is computed in the same way as for the single-step model, using Equations 17.2-4–17.2-6.

The default constants for the two-step model are for combustion of acetylene (C_2H_2). According to [1], these values should be modified for other fuels, since the sooting characteristics of acetylene are known to be different from those of saturated hydrocarbon fuels.

Nuclei Generation Rate

The net rate of nuclei generation in the two-step model is given by the balance of the nuclei formation rate and the nuclei combustion rate:

\[ \mathcal{R}_{\text{nuc}} = \mathcal{R}_{\text{nuc,form}}^* - \mathcal{R}_{\text{nuc,comb}}^* \] \hspace{1cm} (17.2-10)

where

- \( \mathcal{R}_{\text{nuc,form}}^* \) = rate of nuclei formation (particles \times 10^{-15}/m^3-s)
- \( \mathcal{R}_{\text{nuc,comb}}^* \) = rate of nuclei combustion (particles \times 10^{-15}/m^3-s)

The rate of nuclei formation, \( \mathcal{R}_{\text{nuc,form}}^* \), depends on a spontaneous formation and branching process, described by

\[ \mathcal{R}_{\text{nuc,form}}^* = \eta_0 + (f - g)c_{\text{nuc}}^* - g_0 c_{\text{nuc}}^* N_{\text{soot}} \] \hspace{1cm} (17.2-11)

\[ \eta_0 = a_0 c_{\text{fuel}}^* e^{-E/RT} \] \hspace{1cm} (17.2-12)
Modeling Pollutant Formation

where

\[ c_{\text{nuc}}^* = \text{normalized nuclei concentration} = \rho b_{\text{nuc}}^* \]
\[ a_0^* = a_0/10^{15} \]
\[ a_0 = \text{pre-exponential rate constant (particles/kg-s)} \]
\[ c_{\text{fuel}} = \text{fuel concentration (kg/m}^3\text{)} \]
\[ f - g = \text{linear branching – termination coefficient (s}^{-1}\text{)} \]
\[ g_0 = \text{linear termination on soot particles (m}^3\text{/particle-s)} \]

Note that the branching term, \((f - g)c_{\text{nuc}}^*\), in Equation 17.2-11 is included only when the kinetic rate, \(\eta_0\), is greater than the limiting formation rate \((10^{5} \text{ particles/m}^3\text{-s, by default)}\).

The rate of nuclei combustion is assumed to be proportional to the rate of soot combustion:

\[ R_{\text{nuc,comb}}^* = R_{\text{soot,comb}}b_{\text{nuc}}^* \]
(17.2-13)

where the soot combustion rate, \(R_{\text{soot,comb}}\), is given by Equation 17.2-4.

Effect of Soot on the Radiation Absorption Coefficient

A description of the modeling of soot-radiation interaction is provided in Section 11.3.8.

17.2.3 Using the Soot Models

To compute the soot formation, you will need to start from a converged fluid-flow solution. The procedure for setting up and solving a soot formation model is outlined below, and described in detail on the pages that follow. Remember that only the steps that are pertinent to soot modeling are shown here. For information about inputs related to other models that you are using in conjunction with the soot formation model, see the appropriate sections for those models.

1. Calculate your turbulent combustion (finite-rate or non-premixed) problem using FLUENT as usual.
2. Enable the desired soot formation model and set the related parameters, as described in this section.

   Define → Models → Pollutants → Soot...

3. In the Solution Controls panel, turn off solution of all variables except soot (and nuclei, if you are using the two-step model).

   Solve → Controls → Solution...

4. Also in the Solution Controls panel, set a suitable value for the soot (and nuclei, for the two-step model) under-relaxation factor(s). A value of 0.8 is suggested, although a lower value may be required for certain problems. That is, if convergence cannot be obtained, try a lower under-relaxation value.

5. In the Residual Monitors panel, decrease the convergence criterion for soot (and nuclei, for the two-step model) to $10^{-5}$.

   Solve → Monitors → Residual...

6. Define the boundary conditions for soot (and nuclei, for the two-step model) at flow inlets.

   Define → Boundary Conditions...

7. Perform calculations until convergence (i.e., until the soot—and nuclei, for the two-step model—residual is below $10^{-5}$) to ensure that the soot (and nuclei) field is no longer evolving.

8. Review the mass fraction of soot (and nuclei) with alphanumerics and/or graphics tools in the usual way.

9. Save a new set of case and data files, if desired.

10. If you want to calculate a coupled solution for the soot and the flow field, turn on the other variables again and recompute until convergence. (See the end of this section for some advice on coupled calculations.)
Selecting the Soot Model

You can enable the calculation of soot formation by selecting a soot model in the Soot Model panel (Figure 17.2.1).

![Soot Model Panel]

Figure 17.2.1: The Soot Model Panel

Under Soot Formation Model, select either the One-Step or the Two-Step model. The panel will expand to show the appropriate inputs for the selected model.

(If you want to include the effects of soot formation on the radiation absorption coefficient, turn on the Generalized Model option under Soot-Radiation Interaction.)
### 17.2 Soot Formation

**Setting the Combustion Process Parameters**

For both soot models, you will next define the Process Parameters, which depend on the combustion process that you are modeling. These inputs include the stoichiometry of the fuel and soot combustion and (for the two-step model only) the average size and density of the soot particles:

- **Mean Diameter of Soot Particle** and **Mean Density of Soot Particle** are the assumed average diameter and average density of the soot particles in the combustion system, used to compute the soot particle mass, $m_p$, in Equation 17.2-9 for the two-step model. Note that the default values for soot density and diameter are taken from [149].

  These parameters will not appear when the one-step model is used.

- **Stoichiometry for Soot Combustion** is the mass stoichiometry, $\nu_{\text{soot}}$, in Equation 17.2-6, which computes the soot combustion rate in both soot models. The default value supplied by FLUENT (2.6667) assumes that the soot is pure carbon and that the oxidizer is $O_2$.

- **Stoichiometry for Fuel Combustion** is the mass stoichiometry, $\nu_{\text{fuel}}$, in Equation 17.2-6, which computes the soot combustion rate in both soot models. The default value supplied by FLUENT (3.6363) is for combustion of propane ($C_3H_8$) by oxygen ($O_2$).

### Defining the Fuel and Oxidizing Species

In addition to defining the stoichiometry for the fuel and soot combustion, you need to tell FLUENT which chemical species in your model should be used as the fuel and oxidizer. In the Soot Model panel under Species Definition, select the fuel in the Fuel drop-down list and the oxidizer in the Oxidant drop-down list.

If you are using the non-premixed model for the combustion calculation and your fuel stream, as defined in prePDF, consists of a mixture of components, you should choose the most appropriate species as the Fuel species for the soot formation model. Similarly, the most significant oxidizing component (e.g., $O_2$) should be selected as the Oxidant.
**Modeling Pollutant Formation**

**Setting Model Parameters for the Single-Step Model**

When you choose the single-step model for soot formation, the modeling parameters to be defined are those used in Equations 17.2-3, 17.2-5, and 17.2-6:

- **Soot Formation Constant** is the parameter $C_s$ in Equation 17.2-3.
- **Equivalence Ratio Exponent** is the exponent $r$ in Equation 17.2-3.
- **Equivalence Ratio Minimum** and **Equivalence Ratio Maximum** are the minimum and maximum values of the fuel equivalence ratio $\phi$ in Equation 17.2-3. Equation 17.2-3 will be solved only if $\text{Equivalence Ratio Minimum} < \phi < \text{Equivalence Ratio Maximum}$; if $\phi$ is outside of this range, there is no soot formation.
- **Activation Temperature of Soot Formation Rate** is the term $E/R$ in Equation 17.2-3.
- **Magnussen Constant for Soot Combustion** is the constant $A$ used in the rate expressions governing the soot combustion rate (Equations 17.2-5 and 17.2-6).

Note that the default values for these parameters are for propane fuel [39, 253], and are considered to be valid for a wide range of hydrocarbon fuels.

**Setting Model Parameters for the Two-Step Model**

When you choose the two-step model for soot formation, the modeling parameters to be defined are those used in Equations 17.2-5, 17.2-6, 17.2-9, 17.2-11, and 17.2-12:

- **Limiting Nuclei Formation Rate** is the limiting value of the kinetic nuclei formation rate $\eta_0$ in Equation 17.2-12. Below this limiting value, the branching and termination term, $(f - g)$ in Equation 17.2-11, is not included.
- **Nuclei Branching-Termination Coefficient** is the term $(f - g)$ in Equation 17.2-11.
Nuclei Coefficient of Linear Termination on Soot is the term \( g_0 \) in Equation 17.2-11.

Preexponential Constant of Nuclei Formation is the pre-exponential term \( a_0 \) in the kinetic nuclei formation term, Equation 17.2-12.

Activation Temperature of Nuclei Formation Rate is the term \( E/R \) in the kinetic nuclei formation term, Equation 17.2-12.

Constant Alpha for Soot Formation Rate is \( \alpha \), the constant in the soot formation rate equation, Equation 17.2-9.

Constant Beta for Soot Formation Rate is \( \beta \), the constant in the soot formation rate equation, Equation 17.2-9.

Magnussen Constant for Soot Combustion is the constant \( A \) used in the rate expressions governing the soot combustion rate (Equations 17.2-5 and 17.2-6).

The default values for the two-step model are the same as in [149] (for an acetylene flame), except for \( a_0 \), which is assumed to have the original value from [242]. If your model involves propane fuel rather that acetylene, it is recommended that you change the value of \( \alpha \) to \( 3.5 \times 10^8 \) [1]. For best results, you should modify both of these parameters, using empirically determined inputs for your specific combustion system.

Defining Boundary Conditions for the Soot Model

At flow inlet boundaries, you will need to specify the Soot Mass Fraction, \( Y_{\text{soot}} \), in Equation 17.2-1, and (for the two-step model only) the Nuclei mass concentration, \( b_{\text{nuc}}^* \), in Equation 17.2-7.

Define Boundary Conditions...

You can retain the default inlet values of zero for both quantities or you can input non-zero numbers as appropriate for your combustion system.
**Modeling Pollutant Formation**

**Coupled Soot Calculations**

If you are calculating a coupled solution for the soot and the flow field, you will generally need to increase the convergence criteria for soot (and nuclei, for the two-step model) to $10^{-4}$. You may choose to keep the recommended value of $10^{-5}$ used for the uncoupled soot calculation, but be aware that the coupled solution may not be able to converge to this stricter tolerance.

For coupled calculations you should also use a lower under-relaxation factor for soot (and nuclei, for the two-step model). A value of 0.2 will be suitable in most cases.

If you are calculating a coupled solution and you are modeling radiative heat transfer using a variable absorption coefficient, you should enable the Generalized Model for Soot-Radiation Interaction in the Soot Model panel. When this option is enabled, FLUENT will include the effect of soot on the variable radiation absorption coefficient, as described in Section 11.3.8.

**Reporting Soot Quantities**

FLUENT provides several additional reporting options when your model includes soot formation. You can generate graphical plots or alphanumeric reports of the following items:

- Mass fraction of soot
- Mass fraction of nuclei (for the two-step model only)

Both of these parameters are contained in the Soot... category of the variable selection drop-down list that appears in postprocessing panels.