

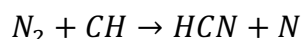
Some Alternative Mechanisms.

Dr Owen Williams – University of Wales TSD:

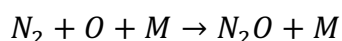
There are generally three mechanisms of NO formation are agreed upon in the literature:

Thermal NO: We have already discussed.

Prompt NO: Produced at the flame front as a result of atmospheric nitrogen reacting with the CH radical (a transient species created during fuel oxidation):



NO via N₂O: The result of oxidation of atmospheric nitrogen, but differs from thermal NO through the presence of any third molecule (*M*):



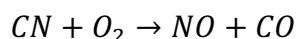
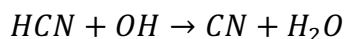
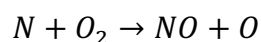
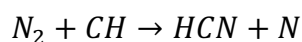
Prompt NO_x.

The presence of a second mechanism leading to NO_x formation was first identified by Fenimore and was termed "prompt NO_x". There is good evidence that prompt NO_x can be formed in a significant quantity in some combustion environments, such as in low-temperature, fuel-rich conditions.

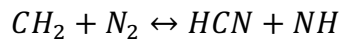
Generally, the prompt NO_x contribution to total NO_x is quite small. However, as NO_x emissions are reduced to very low levels by employing new strategies, the relative importance of the prompt NO_x can be expected to increase.

Prompt NO_x Mechanism

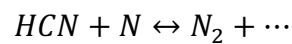
Prompt NO_x is most prevalent in rich flames. The actual formation involves a complex series of reactions and many possible intermediate species. The route now accepted is as follows:



A number of species resulting from fuel fragmentation have been suggested as the source of prompt NO_x in hydrocarbon flames (e.g., CH, CH₂, C, C₂H), but the major contribution is from CH and CH₂, via



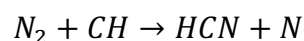
The products of these reactions could lead to formation of amines and cyano compounds that subsequently react to form NO by reactions similar to those occurring in oxidation of fuel nitrogen, for example:



Prompt NO_x Formation Factors

Prompt NO_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_x production increases at first, then passes a peak, and finally decreases due to a deficiency in oxygen.

The reaction:



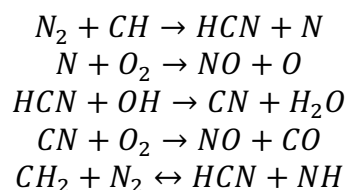
is of primary importance. In recent studies, comparison of probability density distributions for the location of the peak NO_x with those obtained for the peak CH have shown close correspondence, indicating that the majority of the NO_x at the flame base is prompt NO_x formed by the CH reaction. Assuming that reaction above controls the prompt NO_x formation rate,

$$\frac{d[NO]}{dt} = k_{(0)}[CH][N_2]$$

There are, however, uncertainties about the rate data for the above reaction.

Modelling Strategy

From reactions:



it can be concluded that the prediction of prompt NO_x formation within the flame requires coupling of the NO_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 computational NOx models (Fluent – Chemkin), a global kinetic parameter derived by De Soete is used.

De Soete compared the experimental values of total NOx formation rate with the rate of formation calculated by numerical integration of the empirical overall reaction rates of NOx and N₂ formation. He showed that overall prompt formation rate can be predicted from the expression

$$\frac{d[NO]}{dt} = (\text{overall prompt NOx formation rate}) - (\text{overall prompt N}_2\text{ formation rate})$$

In the early stages of the flame, where prompt NOx is formed under fuel-rich conditions, the O concentration is high, and the N radical almost exclusively forms NOx rather than nitrogen. Therefore, the prompt NOx formation rate will be approximately equal to the overall prompt NOx formation rate:

$$\frac{d[NO]}{dt} = k_{(pr)}[O_2]^a[N_2][Fuel]e^{-\frac{E_a}{RT}}$$

For C₂H₄ (ethylene)-air flames,

$$k_{pr} = 1.2 \times 10^7 \left(\frac{RT}{p}\right)^{a+1}$$

where

$$E_a = 251151 \text{ J/gmol}$$

and 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 NOx 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

The equation $\frac{d[NO]}{dt} = k_{(pr)}[O_2]^a[N_2][Fuel]e^{-\frac{E_a}{RT}}$ was tested against the experimental data obtained by Backmier et al., 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 NOx 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.

The equation now becomes

$$\frac{d[NO]}{dt} = f k'_{(pr)} [O_2]^a [N_2] [Fuel] e^{-\frac{E_a'}{RT}}$$

so that the source term due to prompt NOx mechanism is

$$S_{prompt,NO} = M_{\omega,NO} \frac{d[NO]}{dt}$$

In the above equations,

$$f = 4.75 + 0.0819n - 23.2\phi + 32\phi^2 - 12.2\phi^3$$

$$k'_{pr} = 6.4 \times 10^6 \left(\frac{RT}{p}\right)^{a+1}$$

$$E'_a = 303474.125 \text{ J/gmol}$$

n is the number of carbon atoms per molecule for the hydrocarbon fuel, and ϕ 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 were developed at the Department of Fuel and Energy at The University of Leeds in England.

However, since the contribution of prompt NOx to the total NOx emission is often very small, results are not likely to be significantly biased.

Fuel NO_x Formation

Fuel-Bound Nitrogen

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. 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_x is dependent on the local combustion characteristics and the initial concentration of nitrogen-bound compounds. Fuel-bound compounds that contain nitrogen 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, NH₃, N, CN, and NH can be formed and converted to NO_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. Although the route leading to fuel NO_x formation and destruction is still not completely understood, different investigators seem to agree on a simplified model:



Recent investigations 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 **ANSYS FLUENT** NO_x model, sources of NO_x emission for gaseous, liquid and coal fuels are considered separately. The nitrogen-containing intermediates are grouped as HCN, NH₃, or a combination of both.

NO_x Formation from Intermediate N₂O

Melte and Pratt proposed the first intermediate mechanism for NO_x formation from molecular nitrogen (N₂) via nitrous oxide (N₂O). Nitrogen enters combustion systems mainly as a component of the combustion and dilution air.

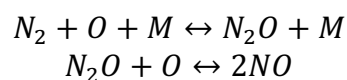
Under favourable conditions, which are elevated pressures and oxygen-rich conditions, this intermediate mechanism can contribute as much as 90% of the NO_x formed during combustion. This makes it particularly important in equipment such as gas turbines and compression-ignition engines. Because these devices are operated at increasingly low temperatures to prevent NO_x formation via the thermal NO_x mechanism, the relative importance of the N₂O intermediate mechanism is increasing. It has been observed that about 30% of the NO_x formed in these systems can be attributed to the N₂O intermediate mechanism.

The N₂O intermediate mechanism may also be of importance in systems operated in flameless mode (e.g., diluted combustion, **flameless combustion**, flameless oxidation, and FLOX systems). In a flameless mode, fuel and oxygen are highly diluted in inert gases so that the combustion reactions and resulting heat release are carried out in the diffuse zone. As a consequence, elevated peaks of temperature are avoided, which prevents thermal NO_x.

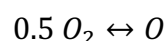
Research suggests that the N₂O intermediate mechanism may contribute about 90% of the NO_x formed in flameless mode, and that the remainder can be attributed to the prompt NO_x mechanism. The relevance of NO_x formation from N₂O has been observed indirectly, and theoretically speculated for a number of combustion systems and by a number of researchers.

N₂O Intermediate NO_x Mechanism

The simplest form of the mechanism takes into account two reversible elementary reactions:



Here, M is a general third body. Because the first reaction involves third bodies, the mechanism is favoured at elevated pressures. Both reactions involve the oxygen radical O, which makes the mechanism favoured at oxygen-rich conditions. While not always justified, it is often assumed that the radical O atoms originate solely from the dissociation of molecular oxygen,



According to the kinetic rate laws, the rate of NO_x formation via the N₂O intermediate mechanism is

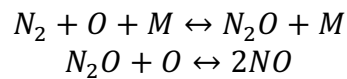
$$\frac{d[NO]}{dt} = 2(k_{f,2}[N_2O][O] - k_{r,2}[NO]^2) \quad \text{gmol/m}^3\cdot\text{s}$$

To solve this, you will need to have first calculated [O] and [N₂O].

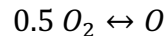
It is often assumed that N₂O is at quasi-steady-state, (i.e., $\frac{d[N_2O]}{dt} = 0$), which implies

$$[N_2O] = \frac{k_{f,1}[N_2][O][M] + k_{r,2}[NO]^2}{k_{r,1}[M] + k_{f,2}[O]}$$

The system of equations above, can be solved for the rate of NO_x formation when the concentration of N₂, O₂, and M, the kinetic rate constants for equations

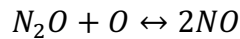


and the equilibrium constant



are known.

The appearance of NO in



entails that coupling of the N₂O mechanism with the thermal NO_x mechanism (and other NO_x mechanisms).

$$k_{f,1} = 4.44 \times 10^{32} T^{-8.358} e^{-2}$$

$$k_{f,2} = 2.9 \times 10^7 e^{-\left(\frac{11651}{T}\right)}$$

$$k_{r,1} = 4 \times 10^8 e^{-\left(\frac{28234}{T}\right)}$$

$$k_{f,1} = 1.45 \times 10^{-29} T^{9.259} e^{-1}$$

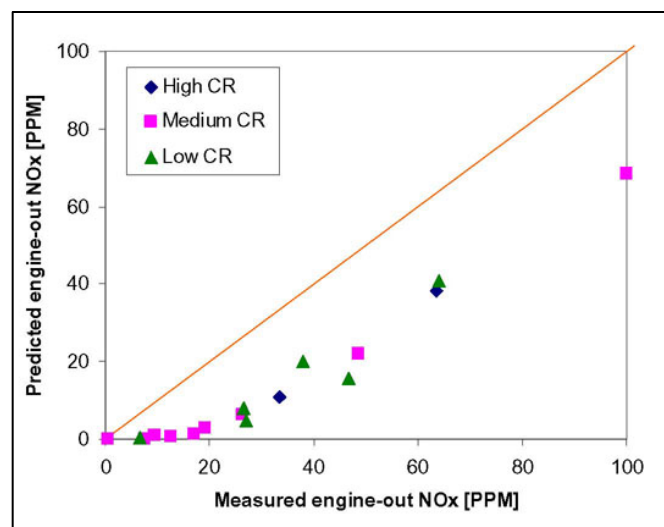
In the above expressions, $k_{f,1}$ and $k_{f,2}$ are the forward rate constants and $k_{r,1}$ and $k_{r,2}$ are the corresponding reverse rate constants. The units for $k_{f,2}$, $k_{r,1}$, and $k_{r,2}$ are m³/gmol.s, while $k_{f,1}$ has units of m⁶/gmol².s.

A Short Literature Review.

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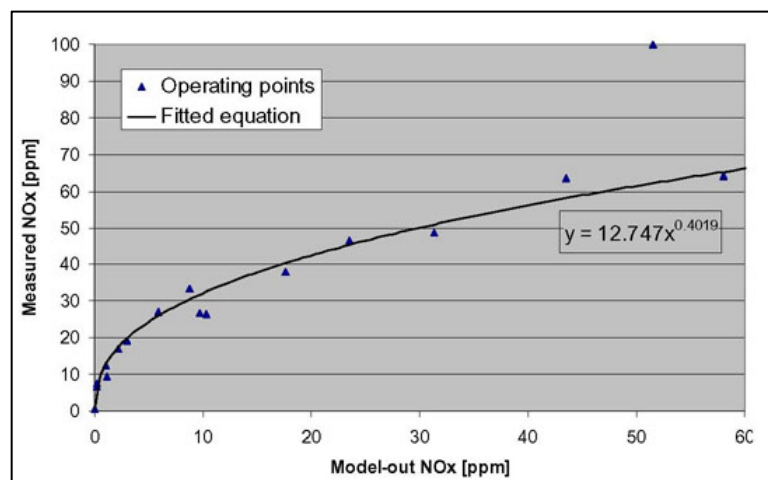
Several authors outline limitations in sole use of the Zeldovich model for NO_x prediction because of its inadequacy at low temperatures, where NO formed from other mechanisms is prevalent.

Andersson et al (2009) presents a semi-empirical Zeldovich model that shows compliance against real data, except in situations of high EGR percentage. EGR used in the test engine reduces combustion temperatures, resulting in low prediction of NO. In these conditions, prompt and N₂O NO are dominant but not accounted for in the model, hence underprediction.



Predicted vs Measured NO_x at high EGR% sites (Andersson et al, 2006)

A previous study from the same authors outlines a simple curve fit method by plotting measured NO_x against modelled NO_x. From this, a correction algorithm is extracted that is employed to burned zone calculations at the end of a cycle when modelled NO_x < 60 PPM:

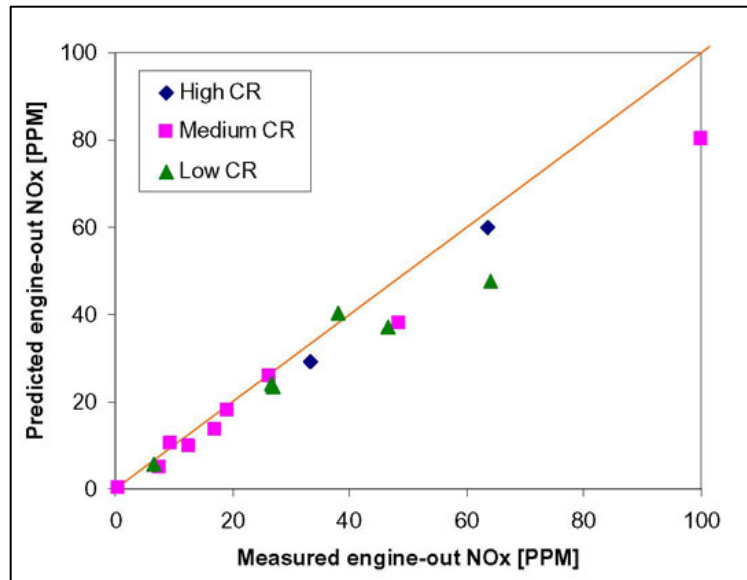


Correction algorithm (Andersson et al, 2006)

Correction is then described for the previous study in the form:

$$ppmNO_{corr} = 12.747 \cdot (ppmNO_{uncorr})^{0.4019}$$

Employment of the same method for the newer study shows good correction but requires engine specific calibration.



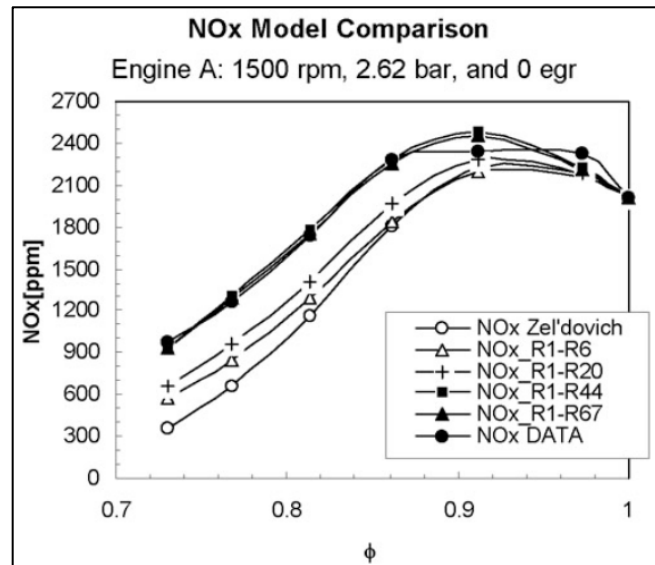
*Predicted vs Measured NOx at high EGR% sites,
employing correction algorithm (Andersson et al, 2006)*

The study goes on to show good agreement of the Zeldovich model down to temperatures of 2300K, at which point deviation from measured NO occurs as another mechanism becomes prevalent. The exact mechanism is though, unfortunately, difficult to identify.

Miller et al (1997) argues that the extended Zeldovich mechanism is not comprehensive enough in its identification of reactions that contribute to NO formation, citing errors of more than 50% when compared to measured engine data.

In response to these failings, Miller et al expanded the mechanism to include 13 chemical species and 67 reactions that either directly or indirectly lead to the formation of NO and are said to dominate NO_x production.

This is dubbed the super extended Zeldovich mechanism (SEZM).

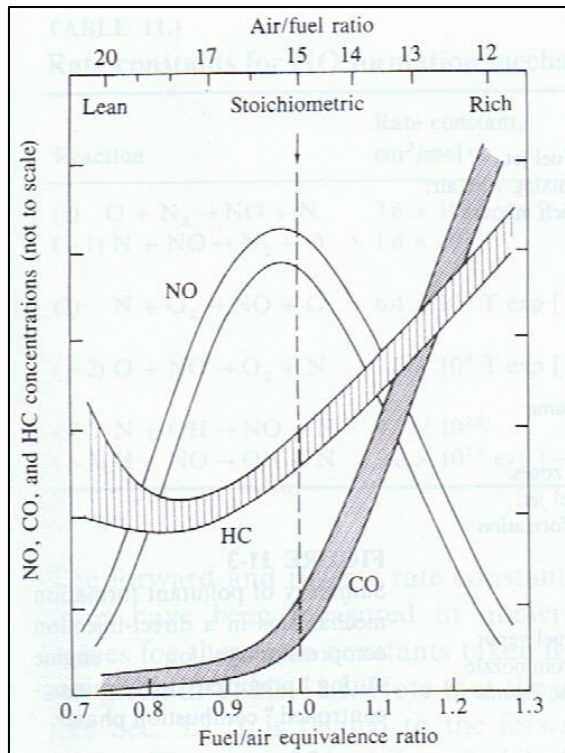


NO_x vs Fuel Equivalence Ratio, for varying degrees of SEZM implementation, where R denotes which reactions out of the 67 were used (Miller et al, 1998)

The figure above shows increasing accuracy as more of the 67 reactions are considered to produce NO_x. Of particular note in this study is the extended Zeldovich mechanism inability to accurately predict NO levels in lean conditions, where temperatures are typically lower and less capable of dissociating the stable N₂ molecule.

Research so far would indicate that prompt or N₂O mechanisms are responsible for this discrepancy. The increased accuracy of the SEZM seems to find some agreement with this observation, including reactions that form NO by way of N₂O in the 67 used.

Also, of note in this study is the required initial calibration of NO production for the SEZM using measured data. Reasons given relate to agreement for reaction rates used and, more notably, to overcome the assumption of mixture homogeneity inherent in the calculations.



Variation of combustion products in terms of Fuel Equivalence Ratio (Heywood, 1988, p571)

An investigation carried out to model NO_x in a stratified charge spark ignition engine by Stone et al (2002) sheds further light on this, noting a GDI engine is capable of unintentionally producing a non-homogenous air/fuel mixture by its very design.

The figure above shows peak NO_x concentration is experienced at slightly leaner than stoichiometric FER, where the trade-off between temperature and available O_2 is optimum for production.

By dividing the burned zone into 10 zones of varying FER that equate to an overall average FER, the study finds that NO_x produced locally in stratified regions does not equate to levels that would be indicative of the average FER.

And there we have it... Enough about NO_x

Merry Christmas!!

