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A numerical study on the formation of NOx in the combustion of iron powder

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A numerical study on the formation of NO\textsubscript{x} in the combustion of iron powder

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Abstract

Metal fuels provide a promising future as replacements for fossil fuels, due to their high energy densities and cost-effectiveness. Iron powder combustion is similar to the combustion of fossil fuels. The iron oxide produced by the combustion of iron particles can be turned back into iron powder, thus making this process a cyclic process. Next to the iron oxide, other species are also formed. However, due to the lack of carbon molecules, harmful CO$_2$ are not among the emissions. Iron flames do produce nitrogen oxide, which could have a detrimental effect on the climate. Therefore, this report investigates the formation of NO in iron flames.

The combustion process is numerically modeled using a version of CHEM1D that is suitable for heterogeneous combustion. The Zeldovich mechanism for producing NO is deemed to be the most important mechanism in forming harmful nitrogen oxides since NO is the most abundant nitrogen oxide and the building block for other, more detrimental, nitrogen oxides. The Zeldovich mechanism is the most important mechanism for forming NO, due to the Fenimore mechanism being inactive due to the lack of hydrocarbons.

It has been found that the most NO is formed between equivalence ratios 0.75 and 1, with a peak at 0.95. The particle size also affects the NO production, due to larger particles having a lower velocity, thus remaining longer in a fixed-length combustion chamber.

Separate simulations using a plug flow of air at maximum particle temperatures show that the majority of the NO for an equivalence ratio lower than 0.75, is formed in the film layers around the particle. The effect of particle size on the NO production in the film layers is less significant for particle sizes larger than 10 [$\mu$m].

Department of Mechanical Engineering, Eindhoven University of Technology
Contents

List of symbols

1. Introduction 1

2. Methods 3
   2.1 NOx formation 3
   2.2 The model 4
   2.3 Effect of film layer 6

3. Results 8
   3.1 Iron flame simulations 8
   3.2 Film layer simulations 9

4. Discussion 13
   4.1 Estimation of NO in film layer model 13
   4.2 Effect of humid air 13
   4.3 Experimental validation of numerical results 13

5. Conclusions 14

References 15

A Simulation Settings 17

B Film layer model results 18
# List of symbols

<table>
<thead>
<tr>
<th>Sign</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h_c$</td>
<td>Chemical heat release of combustion</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_{i,k}$</td>
<td>Kronecker delta</td>
<td>-</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Conductive heat coefficient in the gas</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>$\rho_{O_2,g}$</td>
<td>Density of oxygen in the gas</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{O_2,s}$</td>
<td>Density of oxygen at the particle surface</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Fuel-equivalence ratio</td>
<td>-</td>
</tr>
<tr>
<td>$\omega_i$</td>
<td>Source term for species $i$</td>
<td>kg/(m$^3$s)</td>
</tr>
<tr>
<td>$A_d$</td>
<td>Effective diffusive area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_p$</td>
<td>Particle surface area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_r$</td>
<td>Effective reactive area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity of the particle</td>
<td>J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Heat capacity of the gas</td>
<td>J/(kg K)</td>
</tr>
<tr>
<td>$D_{a*}$</td>
<td>Normalized Damköhler number</td>
<td>-</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Diameter of the (unburned) particle</td>
<td>m</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>$h$</td>
<td>Enthalpy of the gas</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_i$</td>
<td>Unless $i = p$, enthalpy of species $i$</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_{O_2}$</td>
<td>Enthalpy of oxygen in the gas</td>
<td>J/kg</td>
</tr>
<tr>
<td>$H_p$</td>
<td>Total enthalpy of the particle</td>
<td>J</td>
</tr>
<tr>
<td>$h_p$</td>
<td>Mass specific enthalpy of the particle</td>
<td>J/kg</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Pre-exponential factor</td>
<td>m/s</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Heat transfer coefficient</td>
<td>W/(m$^2$K)</td>
</tr>
<tr>
<td>$k_d$</td>
<td>Diffusive reaction rate</td>
<td>m/s</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Surface reaction rate</td>
<td>m/s</td>
</tr>
<tr>
<td>$L_{ei}$</td>
<td>Lewis number of species $i$</td>
<td>-</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass flow of gas</td>
<td>kg/s</td>
</tr>
<tr>
<td>$m_p$</td>
<td>Mass of a particle</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{p,u}$</td>
<td>Unburned mass of the particle</td>
<td>kg</td>
</tr>
<tr>
<td>$n_p$</td>
<td>Number of particles</td>
<td>-</td>
</tr>
<tr>
<td>$\rho_{dens}$</td>
<td>Mixture density of particles in the gas</td>
<td>g/m$^3$</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>Pressure at the inlet</td>
<td>Pa</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>Conductive heat transfer</td>
<td>W</td>
</tr>
<tr>
<td>$Q_m$</td>
<td>Energy transfer due to mass transfer</td>
<td>W</td>
</tr>
<tr>
<td>$R_u$</td>
<td>Universal gas constant</td>
<td>J/(K mol)</td>
</tr>
<tr>
<td>$s$</td>
<td>Spacial coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$S_b$</td>
<td>Gas phase source term for enthalpy exchange</td>
<td>W/m$^3$</td>
</tr>
<tr>
<td>$S_c$</td>
<td>Laminar burning velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$S_{O_2}$</td>
<td>Gas phase source term for oxygen exchange</td>
<td>kg/(m$^3$s)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time coordinate</td>
<td>s</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Temperature of the gas</td>
<td>K</td>
</tr>
<tr>
<td>$T_{g,in}$</td>
<td>Gas temperature at the inlet</td>
<td>K</td>
</tr>
<tr>
<td>$T_p$</td>
<td>Temperature of the particle</td>
<td>K</td>
</tr>
<tr>
<td>$T_{p,max}$</td>
<td>Maximum temperature of the particle</td>
<td>K</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>Reference temperature of enthalpy</td>
<td>K</td>
</tr>
<tr>
<td>$V_{film}$</td>
<td>Volume of the film layer</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_g$</td>
<td>Volume of the gas surrounding the particle and film layer</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Volume of a particle</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$Y_b$</td>
<td>Burned mass fraction of the particle</td>
<td>-</td>
</tr>
<tr>
<td>$Y_i$</td>
<td>Unless $i = b$, mass fraction of species $i$ in the gas</td>
<td>-</td>
</tr>
</tbody>
</table>
1 Introduction

The greenhouse gasses emitted in the past and near future will have irreversible effects for centuries to millennia [1] is one of the many conclusions in the sixth assessment report from the International Panel on Climate Change. Another conclusion from this report is that climate change is definitely caused by the human race. Figure 1.1b shows two types of simulations, one with human factors and one without, compared to observed data. The results clearly show the magnitude of the human influence (Figure 1.1b) and the exponential warming of the planet in the last two centuries (Figure 1.1a). As a response to this report, at the COP26 Conference in Glasgow, 137 countries promised to end deforestation by 2030, 6 major car manufacturers promised to only produce zero-emission vehicles from 2035 onwards, and many more measures were promised [2].

Figure 1.1: Changes in global surface temperature relative to 1850-1900 [2]

In 2020, 83.1% of the energy generated came from fossil sources, whilst only 12.6% is generated from renewable sources (The other 4.3% is from nuclear energy) [3]. One of the reasons why the share of renewable energy is so low is due to the lack of efficient and cost-effective alternatives for fossil fuels in industrial processes. One of the proposed alternatives is the use of metal fuels [4]. Bergthorson et al. envision a metal fuel cycle, where metal is combusted and turned into metal oxide, which in turn can be recycled back to metal using third-party renewable energy. Figure 1.2 shows a schematic of this metal fuel cycle.

Figure 1.2: Schematic of the metal fuel cycle from [5]. In this figure, F represents a metal and FₙOₙ represents a metal oxide.

The advantages of using metal fuels are their high energy densities and abundance in nature. However, metal fuels are a lot less studied than fossil fuels, creating a knowledge gap. On a macro scale, metal fuels can be burned in a similar way as fossil fuels. Iron is particularly suited option for metal flames.
due to its abundance, ease of storing and transport, safety, established market and cost-effectivity. One of the major benefits of metal fuels is their lack of carbon, which makes for almost no CO$_2$ emissions. Although there are (almost) no CO$_2$ emissions in iron flames, there will still be nitrogen oxides emitted. These nitrogen oxides are formed, due to the flame temperatures, from the nitrogen and oxygen in the air. Nitrogen oxides are harmful to the environment since they cause acid rain, global warming and form tropospheric ozone [6].

There is still a lot unknown about the formation of nitrogen oxides in iron flames, therefore, this report will identify the important nitrogen oxides, explain their formation and discuss their numerically modeled emissions. Chapter 2 will explain the model and its important parameters. Chapter 3 will consist of simulation results and findings. The final two chapters will be a discussion and evaluation of the used methods and a conclusion.
2 Methods

This section will explain the theoretical background of this project. First, the formation of nitrogen oxides will be explained, followed by an explanation of the numerical models that are used.

2.1 NO\textsubscript{x} formation

In order to understand and simulate the formation of nitrogen oxides during the combustion of iron powder, it is necessary to identify the harmful nitrogen oxides and understand their formation. The Clean Air Technology Center of the United States Environment Protection Agency identifies several groups of nitrogen oxides, that are detrimental to the environment [6]. These are NO\textsubscript{x} (consisting of NO and NO\textsubscript{2}), N\textsubscript{2}O (sometimes categorized under NO\textsubscript{x}) and nitric- and nitrous acid (HNO\textsubscript{3} and HNO\textsubscript{2} respectively.)

Nitric oxide (NO)

Nitric oxide (NO) in itself is not as detrimental to the environment as the other molecules mentioned above. However, it quickly oxidizes to NO\textsubscript{2}, which in turn is more harmful [6].

The formation of NO is a well-studied topic and can be divided into three formation routes: the Zeldovich mechanism, the fuel mechanism, and the Fenimore mechanism. There is also a formation route called the N\textsubscript{2}O-intermediate mechanism, which will be explained later in this report. The Zeldovich mechanism (also often called “Thermal mechanism”) takes place at temperatures above 1800 K over a wide range of equivalence ratios [7]. The fuel mechanism describes how nitrogen, which is contained in the fuel, oxidizes to NO once the fuel reacts with the oxidizer [6]. The Fenimore mechanism (also called “Prompt mechanism”) uses hydrocarbon radicals that react primarily with nitrogen molecules. This mechanism causes a significant increase in NO formed in the flame zone of hydrocarbon flames [7].

Since this report investigates iron flames, the fuel mechanism can be neglected due to the absence of nitrogen in the fuel. Similarly, since the fuel does not contain hydrocarbons and air only contains around 0.04 vol% CO\textsubscript{2} [8], the Fenimore mechanism will be ignored as well.

The (extended) Zeldovich mechanism are described by the three reaction equations [7]:

\[
\begin{align*}
    &N_2 + O \leftrightarrow NO + N \quad (2.1) \\
    &O_2 + N \leftrightarrow NO + O \quad (2.2) \\
    &N + OH \leftrightarrow NO + H \quad (2.3)
\end{align*}
\]

The activation energy for reaction 2.1 is relatively large, which is the reason that this mechanism only functions above 1800 K. Next to this, reaction 2.1 is the rate-determining reaction in this mechanism since it is slower than the other reactions. Comparing the timescale of reaction 2.1 to fuel oxidation processes, The NO reaction is slower, which explains the fact that the majority of the thermal NO is produced in the post-flame region.

Nitrogen dioxide (NO\textsubscript{2})

Nitrogen dioxide (NO\textsubscript{2}) is more harmful to nature than NO due to two reasons. Firstly, when it dissolves in water, it forms nitric- and nitrous acid, which forms acid rain. Secondly, it reacts in the (tropospheric) atmosphere to form tropospheric ozone. This is the reason why most often NO\textsubscript{2} emissions are regulated.

NO\textsubscript{2} is primarily formed from NO molecules according to the following three reactions [7]:

\[
\begin{align*}
    &NO + O_2 \leftrightarrow NO_2 + O \quad (2.4) \\
    &NO + OH \leftrightarrow NO_2 + H \quad (2.5) \\
    &NO + HO_2 \leftrightarrow NO_2 + OH \quad (2.6)
\end{align*}
\]

Where the HO\textsubscript{2} in reaction 2.6 is formed by:

\[
H + O_2 + M \leftrightarrow HO_2 + M \quad (2.7)
\]
Formation of NO\textsubscript{x} in iron powder combustion

Where M is any third-body species. The formation of HO\textsubscript{2} only takes place at relatively low temperatures, which means that reaction 2.6 only takes place far away from the flame. Meanwhile, reactions 2.4 and 2.5 form NO from NO\textsubscript{2} at high temperatures; however, at low temperatures, this process reverses, thus forming NO\textsubscript{2}.

Nitrous oxide (N\textsubscript{2}O)

Nitrous oxide (N\textsubscript{2}O, or “laughing gas”) is a relatively inert molecule. However, it can react with stratospheric and tropospheric ozone to form oxygen and NO molecules, which can oxidize to NO\textsubscript{2} as mentioned above. Next to this, N\textsubscript{2}O is also classified as a greenhouse gas, due to its ability to trap heat radiation from Earth. Compared to CO\textsubscript{2} the GWP (Global Warming Potential) is 265 times higher for N\textsubscript{2}O.\textsuperscript{9}

N\textsubscript{2}O is formed by\textsuperscript{7}:

\[ N_2 + O + M \leftrightarrow N_2O + M \quad (2.8) \]

This reaction takes place at relatively low temperatures, due to the relatively low activation energy. When the temperature is increased, N\textsubscript{2}O can react with hydrogen and oxygen radicals to form NO. This is called the N\textsubscript{2}O-intermediate mechanism for NO production.

\[ N_2O + O \leftrightarrow NO + NO \quad (2.9) \]
\[ N_2O + H \leftrightarrow NO + NH \quad (2.10) \]

Nitric- and nitrous acid (HNO\textsubscript{3} and HNO\textsubscript{2})

As mentioned earlier, nitric- and nitrous acid (HNO\textsubscript{3} and HNO\textsubscript{2}) are an important contributor to acid rain. These acids are formed when NO\textsubscript{2} molecules react with water:

\[ 3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO \quad (2.11) \]
\[ 2NO_2 + H_2O \leftrightarrow HNO_3 + HNO_2 \quad (2.12) \]

Nitrogen oxide formation in iron flames

As discussed above, the Zeldovich mechanism is the most dominant NO formation route, due to the lack of hydrocarbons and nitrogen-containing fuel. The temperatures in the combustion of iron powder are high enough for the Zeldovich mechanism to take place. The other nitrogen oxides are either formed by or forming NO molecules. Next to this, the concentrations of NO\textsubscript{2} and N\textsubscript{2}O are significantly lower in methane flames.\textsuperscript{10} The NO will eventually form NO\textsubscript{2} and N\textsubscript{2}O in the atmosphere. This makes the NO concentration the most important parameter to investigate.

2.2 The model

The numerical solver used in this project is CHEM1D.\textsuperscript{11} Since the combustion of iron is heterogeneous, a particle model and a coupling to the gas phase must be added. The work of Hazenberg\textsuperscript{12} is used for this. The particle model and the particle-gas phase coupling will be explained below for clarity’s sake.

Single particle combustion

To model the combustion of a single particle, a Lagrangian approach is used. A combination of the models defined by Soo et al.\textsuperscript{13} and Sun et al.\textsuperscript{14} is used for this model. A schematic of the mass transfer of this model can be found in Figure 2.1. It is assumed that steps III and IV are infinitely fast. A set of mass transfer equations, energy transfer equations, and closure equations are explained. The mass growth rate is determined by the reaction rate, which is described by an Arrhenius rate:

\[ \frac{dm_p}{dt} = A_r k_r \rho_{O_2,s} \quad (2.13) \]

with:

\[ k_r = k_0 \exp \left( -\frac{E_a}{R \theta T_p} \right) \quad (2.14) \]
In this Equation 2.13 \( m_p \) is the mass of a particle, \( A_r \) is the effective reactive area of the particle, \( \rho_{O_2,s} \) is the density of oxygen at the particle surface. In Equation 2.14 \( k_0 \) is the pre-exponential factor of the reaction rate, \( E_a \) is the activation energy, \( R_u \) is the universal gas constant and \( T_p \) is the particle temperature, which is assumed to be constant.

Since the density of oxygen at the particle surface is an unknown, a relation to the density of oxygen in the gas, which is a known parameter, is needed. To do this, the normalized Damköhler number is used, which relates the reaction rate to the diffusion rate.

\[
\rho_{O_2,s} = \rho_{O_2,g} \frac{A_d k_d}{A_r k_r + A_d k_d} \quad (2.15)
\]

\[
D a^* = \frac{A_r k_r}{A_r k_r + A_d k_d} \quad (2.16)
\]

\( \rho_{O_2,g} \) denotes the oxygen density in the gas, \( A_d \) is the effective diffusive area, and \( k_d \) is the diffusive reaction rate, which can be calculated if no Stefan flow is assumed. Filling Equation 2.15 and 2.16 in Equation 2.13 gives:

\[
\frac{d m_p}{dt} = A_d k_d \rho_{O_2,g} D a^* \quad (2.17)
\]

Next, the energy transfer equations are solved. The energy transfer consists of a conductive heat flux and an enthalpy exchange, due to the mass transfer of oxygen. The radiative heat flux is neglected. These two heat fluxes are given by Equation 2.18 and 2.19 respectively.

\[
Q_c = k_c A_p (T_p - T_g) \quad (2.18)
\]

\[
Q_m = h_{O_2} \frac{d m_p}{dt} \quad (2.19)
\]

In these equations, \( k_c \) is the heat transfer coefficient, which can be estimated using the Nusselt number, \( A_p \) is the surface area of the particle, \( T_g \) is the temperature of the gas and \( h_{O_2} \) is the specific enthalpy of the (absorbed) oxygen. The total change in enthalpy then becomes:

\[
\frac{d H_p}{dt} = Q_c + Q_m = k_c A_p (T_p - T_g) + h_{O_2} \frac{d m_p}{dt} \quad (2.20)
\]

Finally, to make a set of closed equations, the particle temperature and reactive surface area must be described. Hazenberg [12] assumes a constant heat capacity, in order to determine the particle temperature. This leads to:

\[
T_p = T_{ref} + \frac{\Delta h_c Y_b + h_p}{C_p} \quad (2.21)
\]

with:

\[
Y_b = 1 - \frac{m_p u}{m_p} \quad (2.22)
\]
\[
\frac{dm_{p,u}}{dt} = -\frac{1}{S} \frac{dm_p}{dt}
\]  
(2.23)

\[
h_p = \frac{H_p}{m_p}
\]  
(2.24)

In these equations, \(T_{ref}\) is the reference temperature for the enthalpy, \(\Delta h_c\) is the combustion enthalpy, \(Y_b\) is the burned fraction, \(C_p\) is the heat capacity of the particle, \(m_{p,u}\) is the unburned particle mass, \(S\) is the stoichiometric ratio of kilogram oxygen per kilogram fuel and \(h_p\) is the mass specific enthalphy of the particle.

Since the mass of the particle is known, the area of the particle can be calculated with the assumption that the particle is a sphere. The diffusive area is equal to the particle area, and the reactive area is depended on the amount of empty sites, which is proportional to the burned fraction.

\[
A_d = A_p = \pi d_p^2
\]  
(2.25)

\[
A_r = (1 - Y_p) A_p
\]  
(2.26)

Particle model and gas-phase model coupling

In order to add the particle model to CHEM1D’s gas-phase model, Hazenberg \[12\] uses the work of Filho et al. \[15\]. First, the gas phase is described using the conservation of mass, the conservation of chemical species, and the conservation of energy, which are given by Equation 2.27, 2.28 and 2.29 respectively.

\[
\frac{\partial \dot{m}}{\partial s} = S_{O_2}
\]  
(2.27)

\[
\frac{\partial \dot{m} Y_i}{\partial s} - \frac{\partial}{\partial s} \left( \frac{\lambda}{L_{e_i} c_p} \frac{\partial Y_i}{\partial s} \right) = \dot{\omega}_i + \delta_{i,k} S_{O_2}
\]  
(2.28)

\[
\frac{\partial \dot{m} h}{\partial s} - \frac{\partial}{\partial s} \left( \frac{\lambda}{c_p} \frac{\partial h}{\partial s} \right) = \frac{\partial}{\partial s} \left( \frac{1}{L_{e_i}} \sum_{i=1}^{N} \left( \frac{1}{L_{e_i}} - 1 \right) h \frac{\partial Y_i}{\partial s} \right) + S_h
\]  
(2.29)

In Equation 2.27 \(\dot{m}\) is the mass flux of gas, \(s\) the spacial coordinate and \(S_{O_2}\) the exchange term for oxygen. In Equation 2.28 \(Y_i\) denotes the mass fraction, \(\lambda\) is the thermal conductivity, \(L_{e_i}\) is the Lewis number, \(c_p\) the thermal capacity of the gas, \(\delta_{i,k}\) is the Kronecker delta, with subscript \(k\) referring to the oxygen species, and \(\dot{\omega}_i\) the source term due to gas phase reactions, which are disabled (\(\dot{\omega}_i = 0\)). For all symbols, the subscript \(i\) denotes a certain species. In Equation 2.29 \(h\) is the enthalpy of the gas, \(h_i\) is the enthalpy of species \(i\), \(S_h\) is the energy exchange.

Next, Hazenberg \[12\] describes the tracking of particles using two second-order differential equations. The goal of this tracking is to couple the Lagrangian particle coordinates to the Eulerian spatial coordinates of the gas phase. Lastly, Hazenberg \[12\] explains the method of Filho et al. \[15\] to couple the source terms of the mass and energy transfer between phases.

To reduce the computational time, particles with similar properties are represented with so-called parcels. Since this project uses simulations of flames with constant particle parameters, a single particle representation can be used.

2.3 Effect of film layer

CHEM1D models the NO\(_x\) formation in the gas phase of the iron flames. However, as can be seen in Figure 2.2, the temperature of the iron particle is higher than the gas temperature for lean conditions. This means that there is an increased formation of NO in the film layer around a burning particle.

To find the magnitude of this effect, two steps were performed. First, the size of this film layer is calculated. Second, a simulation is done in air at the film layer temperature to determine the increase of NO production.

To calculate the volume of the film layer, two assumptions have been made. The iron particle (and its film layer) is presumed to be perfectly spherical, and the diameter of the film layer is assumed to be two times the diameter of the (unburned) particle. The volume of the film layer can be computed by:

\[
V_{film} = V_{film+p} - V_p = \frac{7}{6} \pi d_p^3
\]  
(2.30)
The total volume fraction of film layers in the reactor is the volume of all film layers divided by the volume of the gas phase. The volume of the gas phase can be calculated by taking the total volume and subtracting the volumes of all boundary layers and all particles.

\[
\frac{V_{\text{film}}}{V_g} = \frac{\frac{7}{6}n_p\pi d_p^3}{1 - \frac{7}{6}n_p\pi d_p^3}
\]

(2.31)

Where \(n_p\) is the total amount of particles. This value can be computed by dividing the mixture density with the mass of a single particle. Since the mixture density is independent of the \(d_p\) and the mass of a particle, \(m_p\), is proportional to \(d_p^3\), the volume of the film layer (and, therefore, also the volume fraction) is not dependent on the particle size.

\[
n_p = \frac{\rho_{\text{dens}}}{m_p}
\]

(2.32)

The values for the volume fraction of film layers over gas phase volume differ for different mixture compositions. For an undiluted stoichiometric iron-air mixture, the volume fraction is around 0.085 vol\%. This indicates that the volume occupied by the film layers is extremely small as compared to the rest of the gas flow. If, however, the NO production in these film layers is sufficiently large, the effect of the film layer is not negligible. Figure 2.3 shows the relation between equivalence ratio and volume fraction. To find the increased NO formation, a plug flow of hot air is simulated. In these simulations, the particle temperatures from Figure 2.2 are used as the inlet temperatures. The composition of air is taken equal to that of the gas phase of the iron flame simulations. The results from this simulation will be multiplied with the volume fraction and corrected for the time the particle temperature is above the gas temperature. This exact process will be explained in more detail in Chapter 3.2.
3 Results

This chapter will show the simulation results. First, the results of the bulk gas phase simulations are analyzed. First, the flame behavior will be compared to the work of Hazenberg [12], followed by the NO formation for different equivalence ratios and particle sizes. Finally, the results from the bulk gas phase model and the plug flow of air simulations are used to determine the NO formation in the film layer.

The simulation settings used for this chapter can be found in Appendix A. It is decided to use the Syngas/NO_x mechanism, developed at NUI Galway [16], due to its detailed NO_x formation mechanisms.

3.1 Iron flame simulations

Flame behavior

Before a look will be taken at the NO_x emissions, the flame speed and adiabatic flame temperature will be compared to the work of Hazenberg [12] to verify whether the simulations are accurate. Figure 3.1 shows a comparison of the flame speed and adiabatic flame temperature. The results from this project and the work of Hazenberg seem to match, with only a slight difference in magnitude. This difference is most likely due to updates made to the model after the publication of Hazenberg.

NO formation

First, a single case will be investigated, to see how the NO formed in a flame. For this a flame with an equivalence ratio of 0.7 and a particle diameter of 10 \( \mu m \) will be taken. Figure 3.2 depicts the temperature and NO formation over time. In this plot, the point where \( T_g = 1000 \text{ K} \) is taken as \( t = 0 \). The NO formation rate slowly increases once the gas temperatures increases. Once the temperature reaches a steady value, the NO formation rate still increases.

Next, the effect of changing the equivalence ratio and particle size are simulated. For equivalence ratios less than 0.75, the NO formation follows the same trend as depicted in Figure 3.2. With decreasing equivalence ratio, the NO concentration also decreases due to the decline in flame temperature. When the equivalence ratio is above 0.75, the flame temperature reaches a value of 1800 K, thus meaning that the Zeldovich mechanism kicks in. For \( 0.75 < \phi < 1 \), the NO concentration formed is significantly higher than for the equivalence ratios outside this range. This trend follows the trend of the concentration of oxygen radicals. For \( \phi = 1 \) and above, the oxygen radical formation rate decreases after a few milliseconds, thus reducing the NO formation. Figure 3.3a shows the NO concentration for different equivalence ratios at a distance of 10 mm \( T_g = 1000 \text{ K} \) and for 40 ms after the gas temperature has reached 1000 K.

When only the particle size is changed, the flame temperature does not change. From only this information it would make sense to assume that the NO emissions would be the same. However, as Figure 3.3b shows, this is not the case. The velocity of the particles decreases with particle size. This
Formation of NO in iron powder combustion results

Figure 3.2: Temperature profile and NO formation for $\phi = 0.7$ and $d_p = 10 \mu m$.

causes larger particles to be longer in the domain, thus producing more NO in the domain. This means that for combustion chambers with a fixed length, the NO emissions increase sharply for increasing particle sizes. Figure 3.3b shows the NO formation at 10 mm after reaching 1000 K.

Figure 3.3: NO formation for different equivalence ratios and particle sizes

3.2 Film layer simulations

To simulate the NO formation in the film layers, a plug-flow of air, with increased inlet temperatures, is used to find the NO formation in air at elevated temperatures. The output from the simulations from Chapter 3.1 are used to determine the particle temperature and the duration, in which the particle temperature exceeds the gas temperature, for each case. The results from the plug flow simulations at the specified inlet temperature are then corrected for the appropriate volume fraction and duration of particle temperature exceeding gas temperature. For the ease of the reader, this process is explained using $d_p = 10 \mu m$ and $\phi = 0.7$ as an example.

Figure 3.4a shows how the gas temperature and particle temperature change over time in the reactor. The particle temperature obtains a maximum value of 2442 K before dropping and converging with the gas temperature. This peak temperature is used as the inlet temperature for the plug flow simulations. The formation of NO in this plug flow is visualized in Figure 3.4b. However, these results are not accurate estimates for the NO formation in the film layer. This is because the results from the plug flow simulations use the same reactor volume as the results from 3.1 and, thus, have to be corrected for the appropriate volume fraction for film layers. Using Equation 2.31 and 2.32, the volume fraction for a 10 $\mu m$ particle at $\phi = 0.7$ is equal to 0.0593 vol%. Therefore, the results from Figure 3.4b have to be...
Formation of NO in iron powder combustion results

Figure 3.4: Temperature profile and plug flow NO formation for $d_p = 10 \mu m$ and $\phi = 0.7$

multiplied with $5.93 \cdot 10^{-4}$. Next to this, the plug flow simulations are done with a fixed domain size, however, the time a particle temperature exceeds the gas temperature changes under certain conditions. Therefore, the NO formation should be taken at the time the particle temperature exceeds the gas temperature. For the case of $d_p = 10 \mu m$ and $\phi = 0.7$, this time is equal to 5.062 ms. Taking the results from the plug flow simulation and correcting it for the appropriate volume fraction and time results in a NO formation of 11.149 ppm for a 10 $\mu m$ particle at $\phi = 0.7$.

This method is then applied to the simulations with varying equivalence ratios and varying particle sizes. These results are explained in the subsections below.

Varying the equivalence ratio

As Figure 2.2 shows, for lean conditions the particle temperature reaches a higher value than the gas temperature. For rich conditions, the particle temperature does not have a higher peak value than the steady-state gas temperature. Therefore, the NO formation in the film layer is only investigated for equivalence ratios lower than one.

Figure 3.5a shows the NO production from the plug flow simulations with the particle temperatures from Figure 2.2 taken as inlet temperatures. However, as explained above, these results need to be corrected for time $T_p$ is above $T_g$. Figure 3.5b depicts the time where $T_p$ is above $T_g$.

Since the mixture density of particles ($P_{\text{dens}}$) changes for different equivalence ratios, the volume fraction also changes (Figure 2.3). Correcting the results from Figure 3.5a for the time and volume fractions yields
Figure 3.6: These results are fitted with a second-degree polynomial. Appendix B shows how Figure 3.5a changes when the corrections are applied.

Figure 3.6: NO formation in the film layer, corrected for the volume fraction and time $T_p$ exceeds $T_g$ for varying equivalence ratios.

The shape of the curve in Figure 3.6 can be explained by the fact that the peak of Figure 3.5a is shifted towards a higher equivalence ratio, due to the increase in volume fraction for higher equivalence ratios. The time correction decreases the NO formation slightly. An interesting detail to note is that the time correction has a larger effect on the NO formation for higher equivalence ratios. However, for higher equivalence ratios, the maximum particle temperature decreases. For the plug flow simulations, higher inlet temperatures mean the NO concentration reaches a steady value faster. Therefore, the NO formation takes more time to reach a steady concentration for lower temperatures. This means that lower particle temperatures are more dominant than the higher duration of $T_p > T_g$. This outlines the high temperature dependence of the Zeldovich mechanism.

Figure 3.7: Maximum particle and gas temperature (a) and NO formation from the plug flow simulations (b) for varying particle sizes
Varying the particle size

The results from the bulk gas phase model show that the maximum particle temperature changes little for particle sizes larger than 10 \( \mu m \) (Figure 3.7a). The NO formation in the plug flow simulations follows a similar shape, as can be seen in Figure 3.7b. This follows the relation between temperature and NO formation that is seen in other results in this report. The NO formation from Figure 3.7b still needs to be corrected for the volume fraction and duration of \( T_p > T_g \).

The time the particle temperature is above the gas temperature is computed and shown in Figure 3.8b. This relation between particle size and duration of \( T_p > T_g \) is expected. Tang et al. [17] showed that the flame speed, \( s_L \), is proportional to \( 1/d_p \). This relation is observed in Figure 3.8a. It is expected that time relates to the flame speed according to \( t \propto d_p/s_L \). This means that time would scale according to \( t \propto d_p^2 \), which is what is observed in Figure 3.8b.

![Flame speeds for \( \phi = 0.7 \)](image)

![Duration of \( T_p > T_g \) for \( \phi = 0.7 \)](image)

**Figure 3.8:** Flame speed results from the bulk gas phase simulations (a) and the duration in which the particle temperature exceeds the gas temperature (b) for varying particle sizes.

The results from Figure 3.7b have to be corrected for the time from Figure 3.8b and the volume fraction. As explained in Chapter 2.3, the volume fraction does not change for varying particle sizes, with a constant equivalence ratio. Appendix B depicts how the corrections influence the NO formation. The volume fraction decreases the NO formation by a set factor, whilst the time correction has a larger effect on smaller particle diameters, as the duration of \( T_p > T_g \) is less for smaller particles. Figure 3.9 shows the corrected NO formation in the film layer. As can be seen from the figure, the NO formation slowly, but steadily, increases for increasing particle sizes. This is due to the fact that the maximum particle temperature stays almost constant, whilst the duration of particle temperature exceeding gas temperature increases for larger particles.

![Corrected NO formation in film layer for \( \phi = 0.7 \)](image)

**Figure 3.9:** NO formation in the film layer, corrected for the volume fraction and time \( T_p \) exceeds \( T_g \) for varying particle sizes.
4 Discussion

4.1 Estimation of NO in film layer model

The results discussed in Chapter [3.2] are an overestimation of the real formation of NO in the film layer of a particle. This is due to several assumptions made, in order to obtain a ‘worst-case scenario’. Firstly, the temperature gradient in the film layer is not taken into account. The temperature in the film layer is taken to be uniformly equal to the particle temperature. This means that, in reality, the average temperatures in the film layer would be lower, thus reducing the NO formation.

Secondly, the plug flow simulations are only done for the maximum particle temperature obtained. As can be seen in Figure 3.4a, the particle temperature only briefly reaches a maximum value. In this report, the plug flow results are corrected for the entire time the particle temperature exceeds gas temperature. This means that it is assumed that the particle temperature reaches its maximum value instantly and after a certain time reduces instantly towards gas temperature. Since temperature is such an important factor in the formation of NO, it is expected that this assumption has a significant impact on the NO formation results for the film layer.

In this project, the NO formation in film layers for $\phi > 1$ has not been investigated. This is due to the fact that, for rich conditions, the maximum particle temperature is not higher than the flame temperature of the gas. However, for rich conditions, the particle temperature increases faster than the gas temperature, causing a period where the particle temperature exceeds the gas temperature. The duration of this period is significantly shorter for rich conditions than for lean conditions. Combined with the fact that the maximum particle temperature is lower than the gas flame temperature, means that there will still be NO formed in the film layers for rich conditions, but the produced concentration will be significantly smaller than for lean cases.

4.2 Effect of humid air

All simulations done in this report use ‘dry’ air (i.e. no water vapor present). However, in reality, regular air contains a significant amount of water vapor. In The Netherlands, the average relative humidity in 2020 was 77% [18]. This means that, on average, the air at 300 K contains 2.71 vol% water vapor, with a maximum of 3.51 vol% (which is 100% relative humidity). Water molecules in air can dissociate to form oxygen radicals, which are used for Equation 2.1, which is the rate-determining reaction. Therefore, future research on the effect of water vapor on NO formation in iron flames can be conducted.

4.3 Experimental validation of numerical results

This project has only used numerical models to simulate NO$_x$ emissions. Since numerical models are built using numerous assumptions and/or correlations, there are always inaccuracies and differences with real-world phenomena. Therefore, an experimental study on the NO$_x$ emissions in iron flames could provide validation for the numerical work done in this project.
5 Conclusions

The aim of this project was to investigate how NO\textsubscript{x} forms in the combustion of iron powder. A numerical model, describing the combustion of iron particles and reactions in the gas phase, has been used to find the NO\textsubscript{x} formation under different conditions. Since the particle temperature exceeds gas temperature in lean conditions, more nitrogen oxides are formed in the film layer around a particle. These contributions from the film layers to the nitrogen oxide emissions have been investigated as well.

Chapter 2 explained the background of this project, including the formation of NO\textsubscript{x} and an explanation of the model used. This project has focused on the formation of nitric oxide (NO), due to it being important in the formation of other, more harmful, nitrogen oxides and its large formation during combustion.

It has been shown in Chapter 3.1, that for $\phi < 0.75$ there is almost no NO formed. A large peak in NO concentration is found for $0.75 < \phi < 1$. Higher equivalence ratios result again in less NO formed. The peak in NO corresponds with the peak in oxygen radical concentrations for these equivalence ratios. To find out why the oxygen radical concentration peaks at $\phi = 0.95$ a sensitivity analysis can be done to find the underlying phenomena, that are responsible for this peak. Even though the particle size has no effect on the flame temperature, increasing the particle size leads to more NO being formed due to larger particles having a slowing velocity.

The contribution to NO formation in the film layers around the particles has been determined using plug flow simulations of air at high temperatures. Even though the film layers take up a small part (around 0.07 vol\%) of the volume, their increased temperatures cause a significant portion of the total NO emissions. For equivalence ratios less than 0.75, the film layer NO becomes the dominant NO formation source. For $\phi < 0.75$, there is almost no NO formed due to the gas temperature not reaching 1800 K. Therefore, the film layers around the particles are the only area where the Zeldovich mechanism thrives. This results in the most NO being formed in the film layers. It must be noted that the film layer results are an overestimation of the real emissions.

The results from Chapter 3.2 highlight the fact that high temperatures is the most important parameter for the formation of NO. For local temperatures exceeding 1800 K, light increases in temperature result in a significant larger NO production. When the temperatures are more or less constant (e.g. in film layers for particles with varying diameters), the NO formation is much less aggressive.
References


Appendix A  Simulation Settings

Below are the settings for the simulations performed in Chapter 3.1 and 3.2. Table A.1 lists the simulation constants, these parameters never change between simulations. Table A.2 lists the composition of the gas mixture. Similarly, these settings do not change between simulations. Table A.3 lists the parameters that are being changed between simulations to compare their effects. Simulations are never done with multiple parameters changing at once, only one parameter is changed between simulations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>$C_p$</td>
<td>0.677 [J/g K]</td>
</tr>
<tr>
<td>$E_a/R_u$</td>
<td>1.44 · 10^4 [K]</td>
</tr>
<tr>
<td>$k_0$</td>
<td>7.5 · 10^8 [cm/s]</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>1.01325 · 10^5 [Pa]</td>
</tr>
<tr>
<td>$T_{g,in}$</td>
<td>300 [K]</td>
</tr>
<tr>
<td>$\Delta h_c$</td>
<td>2900 [J/g]</td>
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**Table A.1: Simulation parameter settings**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Volume fraction</th>
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<tbody>
<tr>
<td>$N_2$</td>
<td>0.781</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.210</td>
</tr>
<tr>
<td>Ar</td>
<td>0.009</td>
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**Table A.2: Gas mixture composition**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower limit</th>
<th>Step size</th>
<th>Upper limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>0.3</td>
<td>0.01</td>
<td>1.3</td>
</tr>
<tr>
<td>$d_p$</td>
<td>1 [µm]</td>
<td>1 [µm]</td>
<td>70 [µm]</td>
</tr>
</tbody>
</table>

**Table A.3: Variable parameters**
Appendix B  Film layer model results

Figure B.1: NO formation in the film layer, uncorrected and with the corrections applied, for varying equivalence ratios.

Figure B.2: NO formation in the film layer, uncorrected and with the corrections applied, for varying particle sizes.