

Presumed β -PDF Model for the Prediction of the NO_x and CO Emissions in Combustion Chambers

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Abstract

Optimization by means of computational tools has been stunningly useful for different industrial furnaces. However, the complexity of the equations, the wide range of characteristic times in the process, and the difficulty to extract precise enough data to model a combustion chamber hinders the development of a strategy for the reduction of NO_x and CO. Therefore, a simple, computationally cheap, but highly flexible combustion model is desired. All these characteristics can be found in a presumed beta-PDF model. The main advantage of beta-PDF combustion model is that the mass fraction of the number of chemical species can be calculated by just solving transport equations of the mean of the mixture fraction and its variance. A simple squared-2D section with two air inlets and one fuel inlet is built as a test case. Finally, the thermochemical state is defined by a chemistry model based on chemical equilibrium. Every variable is then related to the mixture fraction. By using a presumed probability density function, a more realistic temperature range was found, what is crucial for a proper prediction of the NO_x and CO emission.

Keywords: Probability density function, combustion, furnace, NO_x, emissions

Introduction

Combustion engineering is a technology that through its history and applications has been continuously required to be optimized. Flames are complex processes, which involve more than one hundred reactions occurring in a turbulent-non-isothermal flow. In addition, the variety of types of combustion ranging from continuous operations at industrial furnaces, to batch explosions in car engines, made experimental work an efficient tool to apply to the optimization of combustion systems due to the difficulty of finding the most effective model for each situation ^[1].

The improvement of computers and numerical methods brought to this field several techniques that, together with the proper assumptions can provide reliable descriptions of the flame structure, temperature, composition and other variables. These tools can now be applied in combustion optimization in a more cost-effective way ^[1-3], since running experiments would not be required once the model is validated. Computational optimization has also been found useful to optimize the performance of combustion systems for variables that are difficult to measure at an experimental study, for instance, NO_x and CO concentrations. There are several techniques that can be used in combustion modelling, the most

precise one would be using Direct Numerical Simulations (DNS). This model solves the Navier-Stokes equations without any simplification. DNS offers high precision and resolution, even the small dissipative scales such as Kolmogorov microscales are solved ^[4]. This makes DNS models ideal to proof and validate other simpler models ^[5]. The main counterpart of DNS is the computational cost involved. The non-linear characteristic of the equations and the variety of scales require great computational resources.

Eddy Dissipation Simulations (EDS) are employed, together with a model for the turbulent flow for the computation of infinitely fast chemical reactions ^[6], which would be limited by mixing in a turbulent flow. Commonly, it is used in combination with a RANS or LES model. However, if the chemistry to be studied is complex and includes many chemical species and reaction time scales, the number of equations and complexity of the problem increases. One of the main challenges to properly predict the pollutants concentration in flames is the different time scales between the formation of these species and the main combustion reaction.

The mixture fraction model is an alternative to the previous models which is faster, since only three transport equations are required, and eliminates the

time scales issues by avoiding to compute a reaction term [7]. The structure of the flame is obtained using the extent of mixing between fuel and oxidizer, considering that the diffusivities are equal for all the components involved. The model is built combining the transport equations of the fuel and the oxidizer to get a single variable Z (called mixture fraction). The instantaneous thermochemical state of the mixture is defined just by Z and the enthalpy in a more complex model (The enthalpy balance is not included in this work).

A statistical approach can be added with the inclusion of a probability density function (PDF) [7, 8]. This is normally unknown; however, several experimental works suggest that a β -distribution frequently resembles the characteristics of a combustion system. In addition to the flow equations and the average of the mixture fraction, the variance of the mixture fraction needs to be computed to calculate the required parameters for the PDF.

In this paper, a presumed PDF mixture fraction model was built. The model was applied to a 2D squared furnace with two air inlets and one fuel inlet of the same dimensions. The mass fraction of the gaseous species, the temperature and the density in the furnace were computed with a chemistry model based on the ‘Element Potential Method’. The focus was set on analyzing the obtained temperature field distribution, as well as the responses of the model to changes in the furnace.

Geometry

The main objective was to develop the correct procedure to successfully implement a PDF mixture fraction model in COMSOL® Multiphysics software. For this reason, a geometry as simple as possible was a reasonable option. A 2D open furnace with two air inlets and one fuel inlet was studied. Since there was a symmetry axis, only half the geometry was required. Several designs were studied to check that the model’s results were logical when changes were applied.

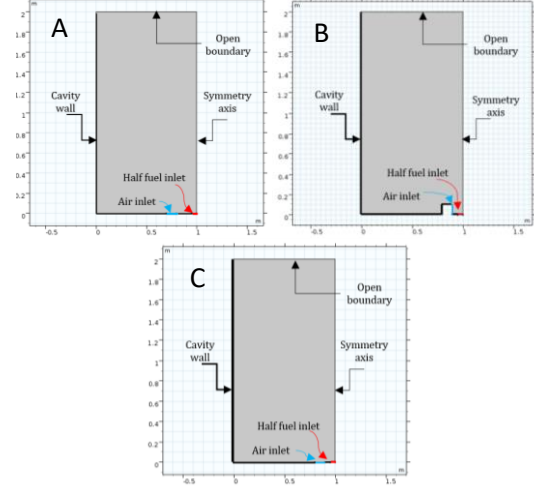


Figure 1. Geometries employed in the study. A: First design. B: Air inlet perpendicular to fuel inlet. C: Air inlet closer to fuel inlet.

The different geometries were supposed to increase the mixing between the oxidizer and the fuel. This was meant to reduce the rich fuel zones resulting in unburnt gases and high concentrations of CO.

Numerical model

Processing stage

The PDF modelling relies on the knowledge of the mixture fraction parameter. According to the definition of the mixture fraction, the balance for the mixture fraction must be derived from the mass balances of the species defined as fuel and oxidizer [7, 9].

$$Z = \frac{\phi \frac{Y_F}{Y_{F,o}} - \frac{Y_O}{Y_{O,o}} + 1}{\phi + 1} \quad \text{Eq. 1}$$

$$\phi = \frac{s \cdot Y_{F,o}}{Y_{O,o}} \quad s = \frac{v_O M_O}{v_F M_F}$$

Modifying the mass balance transport equation for the fuel (In this case modelled as methane) and the oxidizer (In this work modelled as oxygen), the balance for the mixture fraction can be obtained as in Eq. 2. The diffusivity coefficient must be considered constant and equal for all the species, as part of the assumptions of the mixture fraction model.

$$\frac{\partial \rho Z}{\partial t} + \nabla \cdot (\rho u Z) = \nabla \cdot (\rho D \nabla Z) \quad \text{Eq. 2}$$

The mixture fraction model is based on the computation of the mean of the properties of the combustion system in time. More precisely, the outputs should be the mean and the variance of the mixture fraction. Therefore, only steady state solutions of the balances are required.

On this basis, every parameter can be split as seen in Eq. 3, where X is an arbitrary variable, \bar{X} is its mean and X' is its variation in time.

$$X = \bar{X} + X'$$

Applying Eq. 3 to the Eq. 2, Favre averaging all the variables, and employing models for the unclosed terms, the transport equations for the mean and the variance of the mixture fraction can be built (Eq. 4 and Eq. 5)^[7, 10].

$$\nabla \cdot (\bar{\rho} \tilde{Z}) = \nabla \cdot \left(\left(\frac{\mu_T + \mu}{\sigma_T} \right) \nabla \tilde{Z} \right) \quad \text{Eq. 4}$$

$$\begin{aligned} \bar{\rho} \tilde{u} \cdot \nabla [\tilde{Z}'^2] - \nabla \cdot \left(C \frac{\mu_T}{\sigma_T} \cdot \nabla \tilde{Z}'^2 \right) &= \quad \text{Eq. 5} \\ = \nabla \cdot \left(\left(\frac{\mu + 2\mu_T}{\sigma_T} \right) \nabla \tilde{Z}'^2 \right) - 2\bar{\rho} \frac{\epsilon}{k} \tilde{Z}'^2 \end{aligned}$$

The two equations were introduced in COMSOL® Multiphysics software using the ‘Stabilized Convection-Diffusion Equation’ interface from the ‘Mathematics’ module. In addition, the k-ε model for turbulent flow was used as the momentum balance describing the furnace. The required boundary conditions are shown in Table 1.

Table 1. Boundary conditions for the geometry in Figure 1.

Boundary	Flow	\tilde{Z}	\tilde{Z}'^2
Fuel inlet	5 m/s	1	0
Air inlet	$5 \cdot \frac{\phi}{ER}$ m/s	0	0
Furnace wall	Wall B.C.	No flux	No flux
Outlet	$\Delta P = 0$	$\nabla \tilde{Z} = 0$	$\nabla \tilde{Z}'^2 = 0$
Symmetry axis	Symmetry	$\nabla \tilde{Z} = 0$	$\nabla \tilde{Z}'^2 = 0$

Post-processing

Once the transport equations are solved, the probability density function can be defined for each point of the geometry. The value of the

parameters α and β depend on the mean and variance of the mixture fraction.

$$P(Z) = \frac{Z^{\alpha-1}(1-Z)^{\beta-1}}{\int_0^1 Z^{\alpha-1}(1-Z)^{\beta-1} dZ} \quad \text{Eq. 6}$$

$$\alpha = \tilde{Z} \left(\frac{\tilde{Z}(1-\tilde{Z})}{|\tilde{Z}'^2|} - 1 \right) \quad \beta = \alpha \left(\frac{1}{\tilde{Z}} - 1 \right) \quad \text{Eq. 7}$$

The mean and variance of each variable is computed through the calculation of its first and second statistical momentum. It is necessary to know the relation of the variable and the mixture fraction, which is determined by the chemistry model. In Eq. 8 and Eq. 9 this operation is depicted for a random variable ‘ φ ’.

$$\tilde{\varphi}(Z) = \int_0^1 \varphi(Z^+) P(Z^+) dZ^+ \quad \text{Eq. 8}$$

$$\tilde{\varphi}'^2(Z) = \int_0^1 (\varphi(Z^+) - \tilde{\varphi}(Z))^2 P(Z^+) dZ^+ \quad \text{Eq. 9}$$

Chemistry model

The selection of the chemistry model to be used for the post-processing stage will determine the value of each variable. This model must relate the mixture fraction with the mass fraction of all the species of interest, the temperature and the density.

In this work, chemical equilibrium was assumed. Cantera’s tools for MATLAB were employed to solve the equilibrium state of 53 species involved in 325 reactions^[11]. These reactions, and its reaction rate constants were obtained from the GRI-Mech 3.0 database. Cantera’s optimization method for obtaining the chemical equilibrium is the ‘Element Potential Method’^[12]. Since the furnace is open, and the pressure drop at the outlet was assumed to be null, the equilibrium state was solved for an isobaric system at atmospheric pressure. The mixture fraction is calculated from the initial parameters of the system, previous to the equilibrium state calculation.

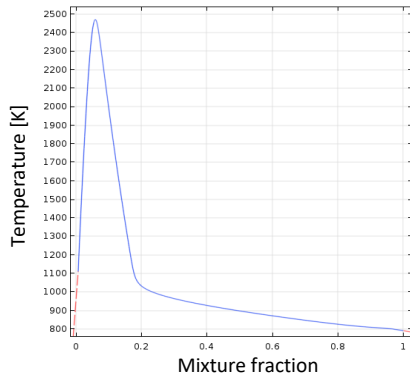


Figure 2. Temperature dependency on the mixture fraction.

As it can be seen in Figure 2, some of the variables of the thermochemical state of the furnace cannot be fit to analytical expressions. Consequently, the values are discretized and introduced in COMSOL® Multiphysics software in interpolation functions.

Methodology

The transport equations for the mixture fraction have a constant of unknown value. The constant σ_T appears in the equation after modelling an unclosed term with the gradient transport hypothesis. This constant is the turbulent Schmidt number, this ranges normally between 0.2 and 1.7^[13, 14].

Since no experimental data was available for choosing the correct value for this constant, a model including the k- ϵ turbulence flow interface, and the interface for the transport of concentrated species was used, without considering any reaction. A mixture fraction was computed from the mass fraction of methane and oxygen. This result was later compared with the solution from the transport equations for different values of σ_T to select the most suitable value.

Parallely, the chemistry model was decided and solved. This had to be done in another software, normally MATLAB or Python. An intermediate software to store the solution might be needed, or the solutions can be introduced in COMSOL® Multiphysics software by adding a 'MATLAB function' in the global definitions section. In this work, both steps were used.

In order to obtain a more realistic solution, it was desired to take into account the effects of a non-isothermal flow. Since no reaction is required for the performance of a mixture fraction model, the

change in the properties of the gas mixture must be related to the Z value at a specific location. The variables affected by the increase of the temperature are density and viscosity. The effect of the latter was considered negligible. To consider the change in the density, the function in the material section was changed for an interpolation function with the results from the chemistry model. When this change is applied, the system is considered coupled.

Reaching convergence when the density is modified by the value of the mixture fraction may be problematic. Using a solution for a system with constant density is an effective way to solve the non-isothermal case.

The procedure required to successfully solve a mixture fraction model using COMSOL® Multiphysics software is depicted in Figure 3.

Once the system is solved, recalculating the mean of the mixture fraction through the first statistical momentum is the best way to check the performance of the PDF model. It was found that the results obtained with the integration routine in COMSOL's operator 'integrate' significantly differed from the results of the transport equation. The main reason is the shape of the β probability density function near the limits, which has an asymptote at 0 if $0 < \alpha < 1$; or at 1 if $0 < \beta < 1$. This difference was found to have a considerable influence in the final calculation of the system variables. For that reason, a MATLAB numerical integration routine was used for this work. The differences between COMSOL transport equations solution and the recalculated Z using 'integrate' (only the best result is shown), and the solution by symbolic integration depending on the lower integration limit can be seen in Figure 4. The values of α and β were chosen from a random point of the system solution ($\alpha=0.0778$, $\beta=4.8691$).

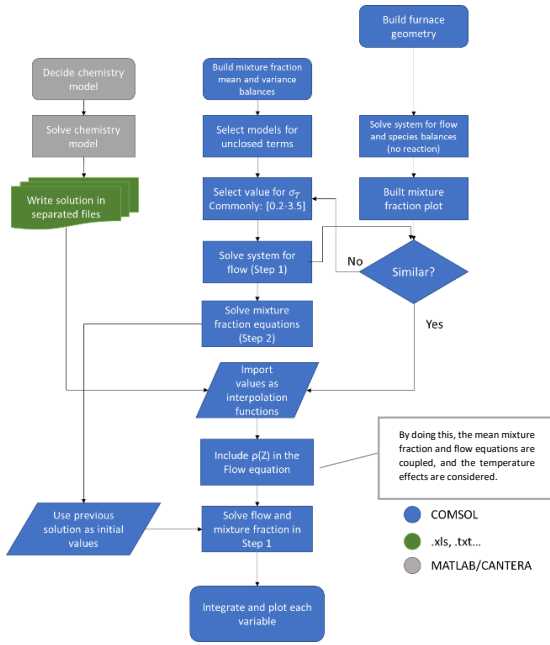


Figure 3. Flowchart describing the procedure to solve a mixture fraction model using COMSOL Multiphysics.

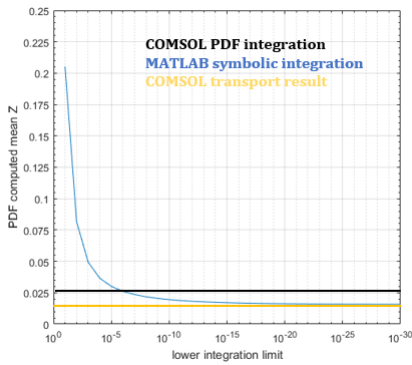


Figure 4. Difference between COMSOL integrate built-in operator and MATLAB symbolic integration for different integration limits.

Results

It was found that the best similarity between the mixture fraction model and the mixture fraction computed from a non-reactive system of methane and air was when σ_T was chosen to be 0.2. A fuel inlet velocity of 5 m/s, an ER=1, and an inlet temperature of 800 K was deliberately chosen to describe the boundary conditions.

It was observed that coupling the flow equation and the mixture fraction balance via the density had a significant influence in the result (See Figure 5)

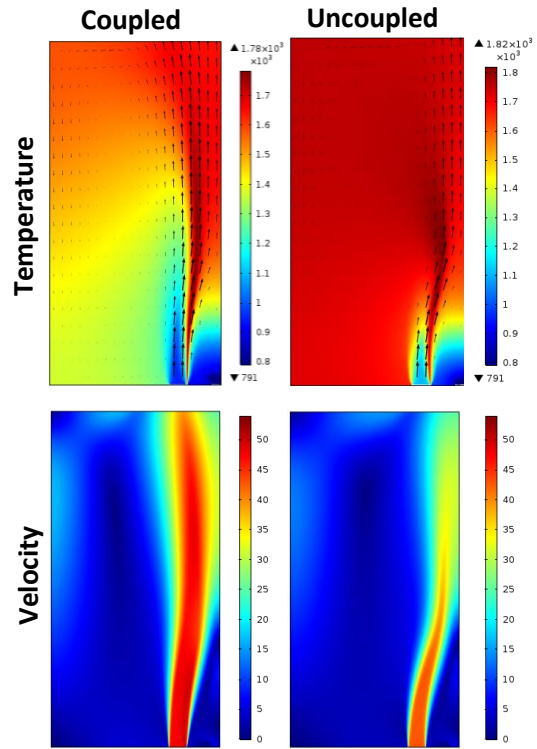


Figure 5. Temperature (Upper row) and velocity (Lower row) field distribution for a coupled (Left columns) and uncoupled (Right columns) mixture fraction model.

As it is observed in Figure 5, the temperature range obtained with the PDF mixture fraction model seems to be more realistic than the one obtained with other simple models. A comparison with a mixture fraction model (without the effect of the PDF) and an EDS model is shown in Figure 7. This improvement is due to consideration of endothermic reactions in the equilibrium model, which were not considered for the EDS model. This is discussed further in the section ‘Temperature profile comparison’. A good estimation of the temperature profile is a key factor for the proper computation of the pollutants being emitted. Mainly due to the strong relation between the thermal NO_x formation and the dissociation of CO₂ in CO and oxygen with the temperature.

Pollutants emissions

The emissions of pollutants in geometry A of Figure 1 were computed by the flux of the species in the open boundary of the furnace (See Eq. 10). The results for different ER are shown in Table 2.

$$Q_i = 2 \int \rho x_i \cdot \mathbf{v} \cdot \mathbf{n} \cdot dl_{open\ boundary} \quad \text{Eq. 10}$$

Table 2. Emissions of the principal pollutants of geometry A for different values of the inlet ER.

Equivalence ratio	CO ₂ emissions	CO emissions	NO _x emissions
	[kg/m ³ s]	[kg/m ³ s]	[kg/m ³ s]
2	0.0712	0.0988	0.00162
1.33	0.0916	0.1018	0.0021
1	0.1076	0.1024	0.00242
0.67	0.1326	0.103	0.00276
0.50	0.1646	0.1198	0.0033

The results from Table 2 can be translated to concentrations in the exhaust gases in the range 2.6-1.6% vol. for CO₂, 5.7-1.8% vol. for CO and 880-465 ppm for NO_x. The values for CO₂ and CO can be considered normal for a combustions system with a poor mixing. However, the NO_x emissions are considered to be up to 10 times higher than expected. The proposed equilibrium model is not suitable for the estimation of the production of thermal NO_x due to the its slow kinetics.

Different geometries were tested in order to verify that the responses of the model to design changes were logical. Different operational conditions were not modelled since they influence the chemistry model, which was not developed in this work.

The high ratio CO/CO₂ is thought to be due to a poor mixing of the fuel and oxidizer streams. The latter is also reflected in the low fraction of the sum of both species, it is lower than the expected result considering the stoichiometric coefficients. Therefore, this is an indication of the presence of unburnt methane. It can be observed that in geometries with a better fuel-oxidizer mixing as in B (perpendicular air-fuel inlets), results closer to a complete combustion of CH₄ were obtained. Figure 6 is an evidence of the poor mixing of geometry A in comparison with B, which has a lower CO/CO₂ ratio, even with higher ER.

Table 3. Pollutants emissions for geometries B and C in comparison with geometry A.

ER	Geometry	CO ₂ emissions	CO emissions	NO _x emissions
		[kg/m ³ s]	[kg/m ³ s]	[kg/m ³ s]
1	A	0.1076	0.1024	0.00242
1	B	0.1234	0.0716	0.00382
0.5	A	0.1646	0.1198	0.00330
0.5	C	0.1590	0.1078	0.00314

The sum of CO₂ and CO mass fractions for geometry B is 12.1% vol., which is a result closer

to that of a system with complete combustion. Defining a smaller distance between the air inlet and the fuel inlet gave very similar results and no significant difference was found between geometry A and C. However, the NO_x concentration in the exhaust gases was found to be too high.

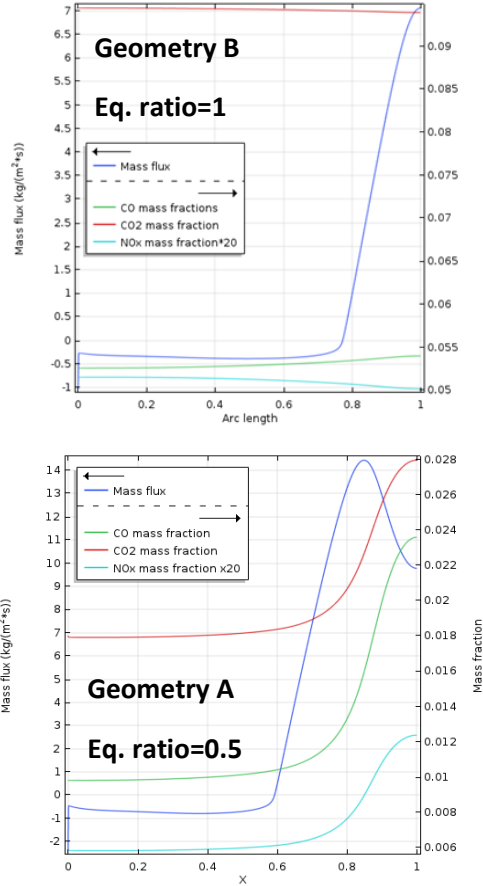


Figure 6. Total flux and mass fraction at the open boundary of geometries A and B for ER of 0.5 and 1 respectively.

Temperature profile comparison

It is thought that one of the most important parameters to be modelled in a combustion system is the temperature. First, because it is the easiest variable to measure at different points in a furnace. This implicates that a model would most probably be validated according to its temperature results. And secondly, because the rest of the variables strongly depend on the temperature. Reaction kinetics and chemical equilibria would be influenced by the temperature profile, this is especially important for the estimation of pollutants such as NO_x and CO.

Simple models as EDS and the mixture fraction model (without the effect of the probability density function) provide overestimations for the temperature. However, the PDF mixture fraction model proposed in this work has a more realistic temperature range, even when adiabatic conditions are assumed to simplify the calculations. This comparison can be seen in Figure 7.

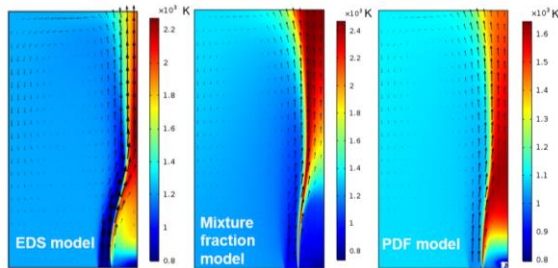


Figure 7. Temperature profile comparison for different combustion models with adiabatic assumption.

Among the different models, different flame shapes can be observed. For the EDS model and the PDF model, higher temperatures are observed near the fuel inlet. In the EDS model this is obtained due to the effect of the energy balance. The temperature in the mixture fraction model is very sensitive to the mixture fraction (See Figure 2), this is solved by contemplating more scenarios with the PDF. Shapes more similar to the EDS solution are obtained with higher values of σ_T .

Conclusions

The present work shows the procedure to develop a presumed PDF mixture fraction model within COMSOL Multiphysics interface. Basically, four steps are required. The first two are parallel, these are obtaining data for the determination of σ_T , preferentially experimental data, and building up the chemistry model. Another software (e.g. MATLAB) is normally required for this step. The third step is the processing stage. Here, the mean and the variance of the mixture fraction are computed from their transport equations. In the final step, post-processing calculations are carried out. For the computation of integrals, it is recommended to use MATLAB numerical integration function due to its better performance near asymptotes.

Since the contribution of more scenarios are taken into account via the PDF, it is also possible to

account for the amount of unburnt fuel. This can be obtained even for simple chemistry models.

Finally, a more realistic temperature range was found due to the ability of the PDF to predict the maximum temperature in a sophisticated way. This is crucial for a proper estimation of the NO_x and CO formation, as well as for the performance of the furnace.

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