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Validation and uncertainty quantification analysis (VUQ) of a char oxidation model

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Abstract: The Reacting Particle and Boundary Layer (RPBL) model computes the transient-state conditions for a spherical, reacting, porous char particle and its reacting boundary layer. RPBL computes the transport of gaseous species with a Maxwell-Stefan multicomponent approach. Mass transfer diffusion coefficients are corrected to account for a non-stagnant bulk flow condition using a factor based on the Sherwood number. The homogeneous gas phase reactions are modeled with a syngas mechanism, and the heterogeneous reactions are calculated with a six-step reaction mechanism. Both homogeneous and heterogeneous reaction mechanisms are implemented in Cantera. Carbon density (burnout) is computed using the Bhatia and Perlmutter model to estimate the evolution of the specific surface area. Energy equations are solved for the gas temperature and the particle temperature. The physical properties of the particle are computed from the fractions of ash, carbon, and voids in the particle. The void fraction is computed assuming a constant diameter particle during the reaction process. RPBL solves a particle momentum equation in order to estimate the position of the particle in a specific reactor. We performed a validation and uncertainty quantification study with RPBL using experimental char oxidation data obtained in an optically accessible, laminar, entrained flow reactor at Sandia National Laboratories. We used a consistency analysis to compare RPBL and experimental data (with its associated uncertainty) for three coal chars over a range of particle sizes. We found consistency for particle temperature and velocity across all experiments.
Keywords: Char oxidation, transient model, homogeneous reaction, heterogeneous reaction, Cantera, multicomponent gas transport, syngas mechanism.

1. Introduction

Char oxidation is a slow process that takes place in the entire domain of a coal-fired boiler. An accurate computation of char oxidation in the entire computational domain is required to predict the O_2 and CO concentrations, particle temperatures (needed for radiative heat flux calculations), and carbon content of the fly ash. Because char oxidation is a complex process, with heterogeneous and homogeneous reactions, species transport, and the evolution of the physical properties of the porous matrix, a high-fidelity model of the process will have many parameters, some of which have high uncertainty.

The Surface Kinetics in Porous Particles (SKIPPY) model, developed by Brian Haynes and coworkers at the University of Sydney [1], and subsequently used by Molina and coworkers [2]

and by Hecht and coworkers [3–6], solves differential equations for the mass fractions of species and for energy inside the particle and in its boundary layer. In this paper we present the Reacting Particle and Boundary Layer (RPBL) model, a transient version of SKIPPY with some additional modifications.

2. RPBL model

RPBL is a one-dimensional model in the radial direction that computes the transient-state conditions for a spherical, reacting, constant-diameter, porous particle and its reacting boundary layer. There are three main components in RPBL: transport of the gaseous species (within the particle and between the particle and the surrounding gas), heterogeneous and homogeneous reactions, and the evolution of physical properties of the porous matrix. The particle and its surrounding gas are considered to be continuous media and there is transport of gas species between them. Therefore, the particle is full of gas. The diffusive transport of species is computed using a multicomponent approach. The porous particle surface has active carbon sites which react heterogeneously with gas species including O_2, CO_2, and H_2O. The heterogeneous reaction rates are computed with Cantera using the reaction mechanism described by Hecht [4, 5]. RPBL model is an intrinsic model because the kinetic reaction rates are computed using the specific surface area. The physical properties of the char particle are dependent on the mass fraction of carbon, which is changing during the reaction process. Additionally, homogeneous reactions can occur between the gas species. The model uses a syngas (H_2/CO) reaction mechanism with 11 species (O_2, H_2O_2, CO, CO_2, O, H, OH, HO_2, HCO, H_2 H_2O) developed by Ranzi and coworkers [7].

This model solves the conservation equations for species mass fractions and energy both inside the particle and in its boundary layer. RPBL uses the same approach as SKIPPY for computing species transport; the source terms are equivalent, but RPBL uses Cantera [8] to compute them while SKIPPY uses CHEMKIN [9] and surface CHEMKIN [10]. RPBL allows a time-dependent boundary condition for all the equations instead of the constant boundary used in SKIPPY. RBPL has two energy equations, one for the particle and one for the gas, while SKIPPY uses a combined energy equation for the gas and particle. Additionally, RPBL has a momentum equation to compute the velocity of the particle separately from the gas velocity. RPBL also accounts for a flowing boundary condition by adding a correction to the stagnant boundary condition used in SKIPPY. SKIPPY uses Darcy's law to compute the pressure inside of the particle; in RPBL we assume a negligible gradient of pressure; Darcy's law is a simplification of the momentum equation for steady state flow in a porous medium, and we are resolving a transient state. Hence, we prefer to assume a negligible pressure gradient and then test the importance of this assumption with experimental data. For a further description of the RPBL see [11].

3. VUQ analysis

We evaluated RPBL using a formal validation and of uncertainty quantification (VUQ) analysis. Our VUQ methodology is a modified version of the Simulator Assessment and Validation Engine framework [12]. This methodology, developed by Schroeder [13], consists of six steps. We present the application of this six step methodology to the RPBL output and the Hecht experiments [5] below.

Selection of quantities of interest: The quantities of interest (QOIs) for this analysis are the particle temperature and velocity data for three char types, two O_2 mole fractions, and six size bins.

Construction of input and uncertainty map: The input and uncertainty (I/U) map is a list of parameters and their associated uncertainty ranges that are being considered in the VUQ analysis. In a previous sensitivity study [11], we identified five sensitive parameters for further analysis: particle diameter (d_p,30-160[μm]), void fraction ($\phi_{initial}$, 0.15-0.7 [$-$]), carbon fraction of the particle (Y_c, 0.15-0.7 [$-$]), particle emissivity (ε_p,0.1-1.0 [$-$]), and the non-dimensional thickness of the boundary layer ($\frac{r_{inf}}{r_p}$, 50.-120. [$-$]). These parameters are known as active parameters; all other parameter values are fixed in the subsequent analysis. A detailed explanation of all the parameters in the I/U map is given in Díaz-Ibarra et al [11].

Data collection (experimental): Hecht [5] produced three chars (obtained from Illinois # 6 ($I6$), Utah Skyline (US), and Black Thunder (BT)) in a high temperature drop tube furnace with an N_2 environment. The char particles were sieved into six narrow size bins of 53-63 μm, 63-75 μm, 75-90 μm, 90-106 μm, 106-125 μm, and 125-150 μm. Hecht tested the sieved char samples in 12 different environments (O_2 $vol\%$ = 24, 36, 60; H_2O $vol\%$ = 10, 14, 16; balance either N_2 or CO_2) in the entrained flow reactor. In each environment for each size bin, Hecht measured the size, velocity and temperature of 100 particles at 3-7 positions in the reactor. We estimated the uncertainty in the experimental data for 36 different experiments (three chars, two environments, six size bins) assuming that the total error was due to sampling error. Sampling error was estimated from the temperature and velocity data that were collected using a t-distribution and a confidence interval of 95 % [14].

Data collection (simulation): We ran a suite of RPBL cases based on five parameters and the requirements of the surrogate model. Given these five parameters and their ranges, we used the Uncertainty Quantification Toolkit (UQTk) [15] to produce a design of experiments. For the O_2 = 24 $vol\,\%$, H_2O = 14 $vol\,\%$, balance CO_2 environment, a polynomial chaos (PC) surrogate model of order 4 with a full quadrature rule required a total of 3125 cases to be run. For the O_2 = 36 $vol\,\%$, H_2O = 14 $vol\,\%$, balance CO_2 environment, a PC surrogate model of order 5 with a full quadrature rule required a total of 7776 cases to be run. We obtained the particle velocity QOI by extracting the velocity at the positions where experimental data were taken. We obtained the particle temperature QOI by computing the average of the cells in the particle (30 in this case) in the same positions.

Construction of surrogate models: We created PC surrogate models [15] for the consistency analysis with the RPBL data. We required a surrogate model because it took one hour of computational time to obtain particle temperature and velocity data from RPBL for one set of parameters. This function evaluation time is too long for the consistency analysis tool, so we pre-computed the particle temperature and velocity with RPBL, then built a surrogate model with these data. We built a PC surrogate model for each measurement type at each position. For example, if the experimental data were taken at five positions, we would build five PC surrogate models for particle temperature and five for velocity.

Analysis of model outputs: This study uses a consistency analysis referred to as bound-to-bound consistency [16] that compares model outputs with experimental data using equation (1). In this equation, $y_{m,e}(x)$ is the model output defined by the set of x parameters, y_e is the experimental data point, and u_e is the experimental uncertainty. If $\Delta \leq 1$, then the model data point using

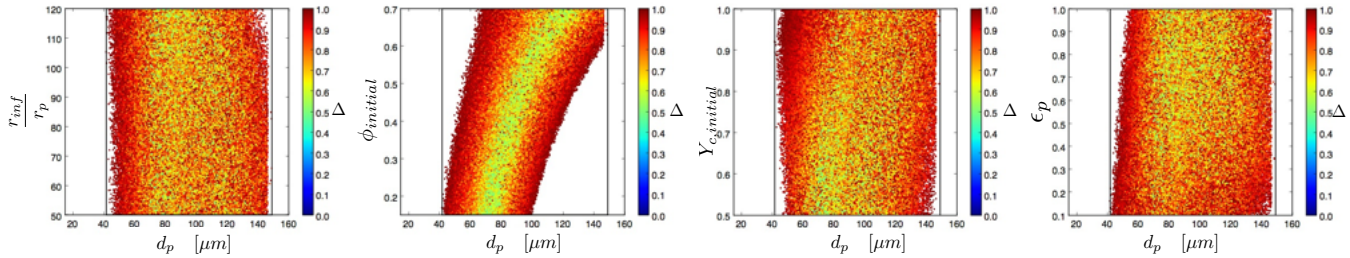

Figure 1: Consistent sample for US char in an O_2 = 24 $vol\%$, H_2O =14 $vol\%$, balance CO_2 environment and 75-90 μm size bin.

Table 1: Parameter ranges prior to and after consistency analysis for US char in an O_2 = 24 $vol\%$, H_2O = 14 $vol\%$, balance CO_2 environment and 75-90 μm size bin

Parameter	Prior range	Consistent range	Nominal value
$d_p\,[\mu m]$	36.9- 146.5	42.0-146.0	75-90
$\phi_{initial}$	0.15 - 0.7	0.15 - 0.7	-
$Y_{c,intial}\,[-]$	0.5-1	0.5-1	-
$\frac{r_{inf}}{r_p}\,[-]$	50-120	50-120	-
$\varepsilon_p\,[-]$	0.1-1	0.1-1	-

parameter set x is consistent with the experimental data point. If the model outputs for a parameter set x are consistent with all the experimental measurements, x is a consistent point in our analysis.

$$\Delta = \frac{|y_{m,e}(x) - y_e|}{u_e} \tag{1}$$

We carried out a consistency analysis for all 36 experiments. Here we describe the consistency analysis for US char in the O_2 = 24 $vol\%$, H_2O = 14 $vol\%$, balance CO_2 environment and the 75-90 μm size bin, but all the analyses were similar.

The consistent points are presented in Figure 1 for one experiment. In this figure, the ranges for the three axes are the original parameter ranges and the box that contains the points is the consistent range. The color of each point corresponds to Δ_{max}, which is the maximum discrepancy (Δ) between the experimental measurements and the model outputs. Table 1 presents the prior and the consistency ranges for this particular consistency analysis.

The nominal value for d_p corresponds to the size bin reported by Hecht [5] (obtained from sieving data). The prior range corresponds to the prior range used in the model and was taken from particle sizes measured in the entrained flow reactor for a given sieving size bin. It is clear from the table data that the particle size variability measured in the entrained flow reactor was much greater than the size range of the unburned char particles based on sieving.

We compare the experimental range (red error bars), simulation range (blue error bars) and consistency range (green error bars) for the temperature and velocity of the particle in Figure 2. In both plots, the consistency range is equal to or smaller than the experimental uncertainty range. The model can reproduce the scatter of particle temperature in all positions. This scatter is mainly due to variation in particle diameter, initial void fraction, initial carbon mass fraction and emissivity.

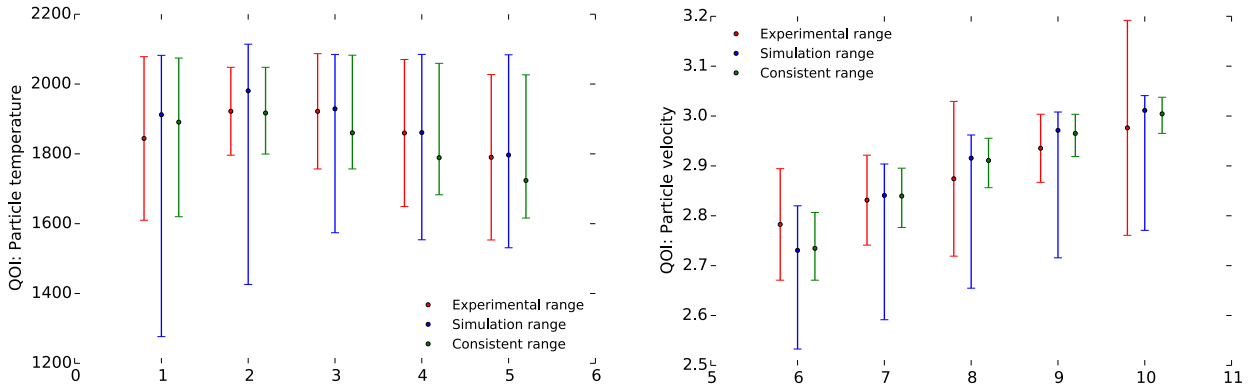

Figure 2: Consistent range for US char in an O_2 = 24 $vol\%$, H_2O = 14 $vol\%$, balance CO_2 environment and 75-90 μm size bin.

Thus, we hypothesize that the large uncertainty in the particle temperatures is due to the large range on particle diameter and the non-constant physical and chemical properties of a single particle. We are able to capture the range of experimental particle velocities because we added a momentum equation for the particle, rather than assuming that same velocity for gas and particle.

We performed a similar consistency analysis for the other experiments and obtained consistency with all 36 experiments.

Feedback and feed-forward: The most important parameter for obtaining consistency was d_p. This parameter determines where the particle is located in the reactor and the amount of total carbon in the particle. RPBL assumes a constant particle diameter during the reaction process. Since we found consistency with all the experimental data, we think that this assumption is adequate. While we use a range of values for $\phi_{initial}$ and $Y_{c,intial}$ in this study, we believe that these parameters must be estimated from a devolatilization model prior to the onset of oxidation.

4. Conclusions

We presented RPBL, a transient model for char oxidation in a spherical particle and in its boundary layer. This model accounts for mass transport of gas species between the particle and the boundary layer using a time dependent boundary condition. Heterogeneous and homogeneous reaction rates are computed with a six-step reaction mechanism and a syngas reaction mechanism respectively.

We followed a six-step methodology to perform a VUQ analysis with the RPBL model output and with experimental data collected by Hecht [5]. The QOIs in this analysis were the particle temperature and velocity. We ran RPBL varying five parameters that showed higher sensitivity to the QOIs; d_p, $\phi_{initial}$, Y_c, ε_p, and $\frac{r_{inf}}{r_p}$. The uncertainty in the experimental data was computed based on sampling error. The consistency analysis between particle temperatures and velocities computed with RPBL and the experimental values was done for 36 groups of data that correspond to three types of char, two gas compositions, and six size bins. Consistency was found for all the 36 groups of data.

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