A Comparative Study of Thermochemistry Models for Oxy-Coal Combustion Simulation

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Abstract

In this work, the One-Dimensional Turbulence (ODT) model is used to evaluate various thermochemistry models for capturing flame stand-off distance in oxy-coal combustion. In the gas phase, calculations made with detailed chemical kinetics are compared with results using an infinitely-fast (flame-sheet) chemistry model. Models for vaporization, devolatilization and char oxidation/gasification are incorporated for each Lagrangian coal particle. Two coal devolatilization models, namely a simple two-step Arrhenius, and Chemical Percolation Devolatilization (CPD), are compared. The governing equations (mass, momentum and energy) are fully coupled between the particle and the gas phase. Flame stand-off distance determined by the simulation is compared with experimental results. Results show that the flame stand-off distance predicted by the infinitely-fast chemistry model is shorter than the prediction obtained by the detailed chemical kinetics model and that flame stand-off distance using two-step model is longer than CPD model. Furthermore, it was observed that the minimum flame stand-off distance is determined by the devolatilization model and does not show sensitivity to the gas phase model. However, the shape of flame stand-off PDF is significantly altered by changing the gas-phase kinetic model.

1 Introduction

Oxy-coal combustion is one of the promising options for CO₂ capture in coal-fired furnaces. Numerical simulation of oxy-coal combustion can improve knowledge of this process and improve design to further increase efficiency while also decreasing greenhouse gas emissions. In this work, different levels of modeling in the gas (carrier) and coal particle (dispersed) phases are compared and analyzed.

The devolatilization process has a considerable impact on the ignition delay of coal particles, and models for devolatilization vary widely in terms of complexity and formulation. The single-rate [1] and two-step [2]

models describe the devolatilization model using one and two Arrhenius-form kinetic rate(s), respectively. The Distributed Activation Energy (DAE) model attempts to account for changes in the structure of coal during devolatilization [3]. These simpler models produce nondescript volatile gas-phase species. Network models treat the devolatilization process as a breakdown of macromolecular networks to produce gas-phase species [4]. Among network models, the Chemical Percolation Devolatilization (CPD) model treats coal as a macromolecular network of aromatic rings that are connected with bridges [5,6]. Jupudi et. al. [7] proposed a more advanced version of the CPD model that determines the yield of light gas species over the course of devolatilization, and is the most advanced devolatilization model considered in this work.

Gas-phase kinetics are frequently treated in a simplified form, relying on the existence of low-dimensional manifolds to describe chemistry by reduced-order models such as flame-sheet, equilibrium, flamelet, *etc.* The flame-sheet model describes the gas phase reactions by a single, infinitely-fast, one-step irreversible reaction, and is among the simplest descriptions of gas-phase chemistry and implies a mixing-limited description of chemistry. Using the “mixed-is-burned” assumption and also accounting for molecular dissociation in the gas phase, the equilibrium model is also a common approach [8,9]. In a furthered advancement, the flamelet model relaxes the infinitely fast chemistry assumption by describing the degree of departure from the equilibrium state using the scalar dissipation rate. The flame-sheet and flamelet models have been applied to simulate ignition of single coal particles [10,11]. In each of these cases, a turbulent closure is typically also included to describe the unresolved fluctuations in composition [12]. Another commonly used model for chemistry modeling in turbulent flow is the Eddy Dissipation Concept (EDC). This model (along with the detailed devolatilization model) has been applied to coal combustion/gasification by Vascellari et. al [13,14]. In any modeling approach, a trade-off between computational cost and fidelity/accuracy is made. This work is investigates the impact of a range of models for both devolatilization and gas-phase chemistry on simulation predictions. Models on both ends of the spectrum of cost/fidelity are compared to experimental data for flame stand-off distance in an oxy-coal system.

To resolve the full range of length and time scales of the continuum as in direct numerical simulation, but at a significantly lower computational cost, Kerstein [15] proposed the One-Dimensional Turbulence (ODT) model. ODT resolves the full range of length and time scales, but in a single direction and the effects of turbulent mixing are modeled. A Eulerian formulation of ODT model that solves evolution of velocity and scalars along a one-dimensional line of sight in a three-dimensional turbulent flow field is applied in this work [16,17]. The capabilities of the ODT model have been previously established for particle-laden flows [18] and turbulence-chemistry interaction (including extinction and reignition) [19,20] and oxy-coal combustion [21].

Previous ODT simulations of a 40 kW oxy-coal combustor [22–24] have examined the impact of system and model parameters on flame stand-off [21]. In [21], detailed gas phase kinetics were paired with CPD devolatilization model. Previous work by the authors has also considered the effect of particle size, environment temperature and coal type for laminar, single-particle scenarios [10]. The aim of this work is to study the impact of chemistry models in coal and gas phases on prediction of flame stand-off. Specifically, we consider pairings of two devolatilization models (CPD and two-step) with two gas-phase chemistry models (detailed kinetics and flame-sheet). The choice of these models covers relatively simple (two-step devolatilization and flame-sheet gas-phase chemistry) to high-fidelity (CPD and detailed gas kinetics) and provides some insight into the effect of model fidelity on flame stand-off predictions.

2 Model Formulation

2.1 Conservation Equations

The governing equations for mass, momentum, energy and species for the gas and the particle phase are presented here. More detail can be found in [10, 16, 17, 21, 25].

2.1.1 Gas Phase

In the gas phase, conservation equations are solved for mass, momentum¹ and energy:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial v}{\partial y} + S_{pm}, \quad (1)$$

$$\frac{\partial \rho v}{\partial t} = -\frac{\partial \rho v v}{\partial y} - \frac{\partial \tau_{yy}}{\partial y} - \frac{\partial P}{\partial y} + S_{pv}, \quad (2)$$

$$\frac{\partial \rho u}{\partial t} = -\frac{\partial \rho v u}{\partial y} - \frac{\partial \tau_{yx}}{\partial y} + S_{pu}, \quad (3)$$

$$\frac{\partial \rho e_0}{\partial t} = -\frac{\partial \rho e_0 v}{\partial y} - \frac{\partial p v}{\partial y} - \frac{\partial \tau_{yy} v}{\partial y} - \frac{\partial q}{\partial y} + S_{pe_0}, \quad (4)$$

$$\frac{\partial \rho Y_i}{\partial t} = -\frac{\partial \rho Y_i v}{\partial y} - \frac{\partial J_i}{\partial y} + \omega_i + S_{pY_i}, \quad (5)$$

where ρ is density, v and u are velocity components in the x and y directions, e_0 is total energy and Y_i is mass fraction of species i . Source terms appearing in the above equations will be defined in §2.4. Equations (1)-(5) are completed by the ideal gas equation of state, $P = \rho RT/M$ and constitutive relationships for the

¹Only two components of momentum are solved here: the component parallel to the ODT direction and the primary streamwise component. See [16, 17] for more information.

diffusive fluxes

$$\tau_{yy} = -\frac{4}{3}\mu\frac{\partial v}{\partial y}, \quad (6)$$

$$\tau_{yx} = -\mu\frac{\partial u}{\partial y}, \quad (7)$$

$$q = -\kappa\frac{\partial T}{\partial y} + \sum_{i=1}^{n_s} h_i J_i, \quad (8)$$

$$J_i = -\frac{\rho Y_i}{X_i} D_i^{mix} \frac{\partial X_i}{\partial y}, \quad (9)$$

where μ and κ are viscosity thermal conductivity; h_i , X_i and D_i^{mix} are the species enthalpy, mole fraction and mixture-averaged diffusivity, respectively. S_{pm} , S_{pv} , S_{pu} , S_{pe0} and S_{pY_i} are particle source terms for mass, y and x velocities, energy and species, respectively, that are described in [10, 21, 25]. Finally, the gas phase temperature is determined from the internal energy, composition and pressure via a newton-solve. In the ODT, stochastic eddy events representing turbulent mixing are modeled in a manner that has been shown to reproduce salient statistics including the $-5/3$ energy cascade [15] as well as extinction and reignition in combustions flows [19].

2.1.2 Particle Phase

On each particle, conservation equations are written for mass, velocity and temperature:

$$\frac{dm_p}{dt} = \frac{dm_{H_2O}}{dt} + \frac{dm_v}{dt} + \frac{dm_c}{dt}, \quad (10)$$

$$\frac{du_p}{dt} = \frac{g_x(\rho_p - \rho_g)}{\rho_p} + S_{p,u}, \quad (11)$$

$$\frac{dv_p}{dt} = \frac{g_y(\rho_p - \rho_g)}{\rho_p} + S_{p,v}, \quad (12)$$

$$\frac{dT_p}{dt} = \frac{-A_p}{m_p C_p} [h(T_p - T_g) + \varepsilon\iota(T_p^4 - T_r^4)] + S_{p,T}, \quad (13)$$

where m_{H_2O} , m_v , m_c are the mass of moisture, volatile and char in the coal particle and m_p is the total mass of particle, u_p and v_p are velocities of particle at x and y directions. T_p , T_g and T_r are particle, gas and effective radiative temperatures. A_p , C_p and ρ_p are particle surface area, heat capacity and density respectively. The convective heat transfer coefficient is represented by h ; also, ε and ι are emission coefficient and Stefan–Boltzmann constant, respectively. Source terms appearing in the above equations will be defined in §2.4.

Additional equations for the composition of each particle are solved depending on the models chosen for vaporization, devolatilization and char oxidation/gasification.

The particle diameters are constant during the simulation and mass conservation equation 10 affects the particle density. Inter-particle interaction and particle swelling are not considered.

2.2 Gas Phase Chemistry

Two different gas-phase chemistry models are considered in this work: detailed kinetics and infinitely-fast (flame-sheet) chemistry. In both models, the species transport is fully coupled with the particle transport. A brief description of these models is given below, with additional details provided in [10].

2.2.1 Detailed Chemistry

To address detailed chemistry in the gas phase, a reduced GRI3.0 mechanism consisting of 24 species and 86 reactions is utilized [26]. This mechanism has also been applied in the previous study [21]. The species mass balance equations 5 are solved for each species and are fully coupled with particle phase.

2.2.2 Flame-Sheet Model

The flame-sheet model employed here has been discussed previously [10,25]. In this model, the transport equations are only solved for the species produced/consumed by the coal sub-models as well as any gaseous species injected into the reactor. The local state of the reacted system (composition, temperature, transport coefficients, *etc.*) is then determined algebraically from the flame-sheet model.

In this model, reactants (r) form products (φ) through an infinitely fast reaction,

$$r_i \rightarrow \varphi_i, \quad (14)$$

where i represents moles of i^{th} species (except O_2) in reactants and flame-sheet product. The local equivalence ratio (Φ) determines the flame-sheet product. For lean conditions ($\Phi \leq 1$), the products are

$$\varphi_i = \begin{cases} E_C^r & i = CO_2 \\ E_H^r/2 & i = H_2O \\ E_N^r/2 & i = N_2 \\ r_{O_2} - \theta & i = O_2 \\ 0 & \text{otherwise} \end{cases} \quad \Phi \leq 1, \quad (15)$$

where θ is stoichiometric oxygen, E_j^r is the amount of element j provided by the reactants,

$$E_j^r = \sum r_i \sigma_{ij} \quad i \neq \text{O}_2, \quad (16)$$

and σ_{ij} is the number of element j in the species i . If the local mixture is rich ($\Phi > 1$), the products are

$$\varphi_i = \begin{cases} r_{\text{CO}_2} + E_C^\pi & i = \text{CO}_2 \\ r_{\text{H}_2\text{O}} + E_H^\pi/2 & i = \text{H}_2\text{O} \\ r_{\text{N}_2} + E_N^\pi/2 & i = \text{N}_2 \\ 0 & i = \text{O}_2 \\ r_i(1 - \Phi \frac{\xi_j}{\sum_j \xi_j}) & \text{otherwise} \end{cases} \quad \Phi > 1, \quad (17)$$

with

$$E_j^\pi = \Phi \sum_i r_i \sigma_{ij}. \quad (18)$$

2.3 Coal Models

In this work, the coal particle consists of moisture, volatile, char and ash as illustrated in Figure 1. For each coal constituent (except for ash, whose mass is assumed constant) a sub-model is developed that describes its mass evolution.

Figure 1: Coal Constituents [10].

The focus of this work is to study the flame physics before ignition, therefore models for tar and soot

formation are not included. Here, a brief description of the coal sub-models is provided. Details of the models can be found in [10, 25].

2.3.1 Evaporation

Moisture content evolution is described by

$$\frac{dm_{\text{H}_2\text{O}}}{dt} = \begin{cases} k_v \left(\frac{P_{\text{H}_2\text{O},\text{sat}}}{RT} - \frac{P_{\text{H}_2\text{O}}}{RT_g} \right) A_p M_{\text{H}_2\text{O}}, & m_{\text{H}_2\text{O}} > 0 \\ 0, & m_{\text{H}_2\text{O}} = 0 \end{cases}, \quad (19)$$

where k_v is the mass transfer coefficient of steam into air [27], $P_{\text{H}_2\text{O},\text{sat}}$ is the saturation pressure of water at the particle temperature, and $P_{\text{H}_2\text{O}}$ is partial pressure of water in the gas phase. The contribution of the evaporation model to the gas-phase species mass source term (equation (5)) is

$$(S_{\text{p},\text{H}_2\text{O}})^{\text{Evap}} = -\frac{dm_{\text{H}_2\text{O}}}{dt}. \quad (20)$$

2.3.2 Devolatilization

The volatile matter has notable influence on ignition delay [10]. As discussed in the introduction, different models are proposed to describe devolatilization process. In this work, the two-step and CPD models are utilized and their predictions are compared.

Two-Step

This model describes devolatilization process through two competing reactions [2],

$$m_v \begin{cases} \nearrow & \alpha_1 g_i^1 + (1 - \alpha_1)c \\ \searrow & \alpha_2 g_i^2 + (1 - \alpha_2)c \end{cases} \quad (21)$$

where $\alpha_1 = 0.3$ and $\alpha_2 = 1.0$ are volatile yield factors, g_i^1 and g_i^2 are the volatile products and c is the char produced by the model. In this formulation, we assume $g_i^1 = g_i^2 = \{\text{CO}, \text{H}_2, \text{C}_2\text{H}_2\}$, where C_2H_2 is serves as soot precursor. This is clearly not realistic, but the results presented herein (examining flame stand-off distance) are relatively insensitive to this approximation.

In terms of the two reactions in (21), the mass evolution of volatiles is

$$\frac{dm_v}{dt} = -(r_1 + r_2)m_v, \quad (22)$$

where $r_i = A_i \exp(-E_i/RT_p)$ with Arrhenius parameters reported in Table 1 [28–30]. The devolatilization

Table 1: Arrhenius parameters for the two-step model reported by [31]

	A (1/s)	E (kcal/kmol)
r_1	3.7e5	17600
r_2	1.46e13	60000

process described in (21) can be summarized as

with

$$\chi = \beta \alpha_1 + (1 - \beta) \alpha_2, \quad (24)$$

$$\Upsilon = \beta(1 - \alpha_1) + (1 - \beta)(1 - \alpha_2), \quad (25)$$

where $\beta = r_1 / (r_1 + r_2)$ and, from an elemental balance, $\varrho = b/\chi$, $\sigma = a/2\chi - \varsigma$, $\varsigma = (\bar{c} - \Upsilon - b)/2\chi$. The values of a , b and $\bar{c}$ are initialized using the coal’s ultimate analysis.

To account for changes in coal composition as devolatilization proceeds, we evolve a , b and $\bar{c}$ according to

$$\frac{da}{dt} = \frac{2\chi}{M_v} (\sigma + \varsigma) \frac{dm_v}{dt}, \quad (26)$$

$$\frac{db}{dt} = \frac{\chi \varrho}{M_v} \frac{dm_v}{dt}, \quad (27)$$

where M_v is the volatile molecular weight. In (23), the carbon coefficient, $\bar{c}$, is determined from a mass balance:

$$\bar{c} = (m_v - aM_H - bM_O) / M_C. \quad (28)$$

The species source terms contributing to (5) from two-step devolatilization model can be described as:

$$(S_{p,CO})^{\text{Dev}} = \chi \varrho \frac{dm_v}{dt} \frac{M_{CO}}{M_v}, \quad (29)$$

$$(S_{p,H_2})^{\text{Dev}} = \chi \sigma \frac{dm_v}{dt} \frac{M_{H_2}}{M_v}, \quad (30)$$

$$(S_{p,C_2H_2})^{\text{Dev}} = \chi \varsigma \frac{dm_v}{dt} \frac{M_{C_2H_2}}{M_v}. \quad (31)$$

Finally, the generation of char from devolatilization is given by

$$\left(\frac{dm_c}{dt}\right)^{\text{Dev}} = m_v [r_1(1 - \alpha_1) + r_2(1 - \alpha_2)]. \quad (32)$$

Chemical Percolation Devolatilization (CPD)

In the CPD model, coal is described as a macromolecular network of aromatic ring clusters of various sizes and types that are connected by a variety of chemical bridges (so-called “labile bridges”) with different bond strengths [5]. Devolatilization starts with decomposing of labile bridges (l) to form highly reactive intermediate bridges (l^*). The reaction proceeds with stabilizing l^* that produce either stable char with the associated light gases, or side chains (δ) that may eventually convert into light gases. This process is represented schematically as

where $g_i = \{\text{CO}_2, \text{CO}, \text{CH}_4, \text{C}_2\text{H}_2, \text{HCN}, \text{NH}_3, \text{H}, \text{H}_2\text{O}\}^2$ are the released light gases by CPD model, and are directly coupled to the gas-phase species transport equations in this work.

The ordinary-differential equations describing the devolatilization process are

$$\frac{dl}{dt} = -k_l l, \quad (34)$$

$$\frac{dc}{dt} = k_c l^* \cong \frac{k_l l}{\kappa_{\delta/c} + 1}, \quad (35)$$

$$\frac{d\delta_i}{dt} = \left[\frac{2\kappa_{\delta/c} k_b l}{\kappa_{\delta/c} + 1} \right] \frac{\xi_i}{\sum_{j=1}^{16} \xi_j} - k_{g_i} \delta_i, \quad (36)$$

$$\frac{dg_i}{dt} = \left[\frac{2\kappa_{\delta/c} k_b l}{\kappa_{\delta/c} + 1} \right] \frac{\xi_i}{\sum_{j=1}^{16} \xi_j} + k_{g_i} \delta_i, \quad (37)$$

where $\kappa_{\delta/c} = \frac{k_{\delta}}{k_c}$ and ξ_i are functional groups, and $k_{g_i} = A_{g_i} \exp\left(\frac{-E_{g_i}}{RT_p}\right)$ where A_{g_i} and E_{g_i} are the pre-exponential factor and activation energy. The activation energy follows a distribution to account for changing bond strengths as devolatilization proceeds [5, 7], and this has been accounted for in the present implementation of the model. The evolution of species into the gas phase from devolatilization for the CPD model is

$$(S_{pY_i})^{\text{Dev}} = \frac{dg_i}{dt} M_i. \quad (38)$$

²For the purposes of this work, we represent the tar produced by CPD as C_2H_2 . We have verified that this has negligible impact on the results presented herein, which are concerned primarily with ignition.

where M_i is the molecular weight of species i . Finally, char is produced as

$$\left(\frac{dm_c}{dt}\right)^{\text{Dev}} = \frac{dc}{dt} M_c, \quad (39)$$

where M_c is the char molecular weight.

2.3.3 Char Oxidation & Gasification

The total char consumption rate appearing in (10) is comprised of devolatilization, oxidation and gasification,

$$\frac{dm_c}{dt} = \left(\frac{dm_c}{dt}\right)^{\text{Dev}} + \left(\frac{dm_c}{dt}\right)^{\text{Oxid}} + \left(\frac{dm_c}{dt}\right)^{\text{Gasif}}, \quad (40)$$

where $\left(\frac{dm_c}{dt}\right)^{\text{Dev}}$ is the production of char as devolatilization proceeds and is given by (32) and (39) for the two-step and CPD models, respectively. The char consumption due to oxidation and gasification in (40) are considered next.

The consumption of char mass due to oxidation in 40 is described using a model proposed by Murphy *et al.* [32],

$$\left(\frac{dm_c}{dt}\right)^{\text{Oxid}} = -\frac{r_c^{\text{Oxid}} M_c}{\varphi} \pi d_p^2, \quad (41)$$

where $\varphi = 2/(1 + \psi)$ is the stoichiometric ratio of carbon consumption, M_c is the molecular weight of carbon and d_p is the diameter of the coal particle. The reaction rate (r_c^{Oxid}) is determined using a suggested form for Langmuir-Hinshelwood model [32]

$$r_c^{\text{Oxid}} = \frac{k_2 k_1 P_{o_2, s}^{n_o}}{k_1 P_{o_2, s}^{n_r} + k_2}, \quad (42)$$

where $n_o = 0.32$ and the Arrhenius parameters for k_1 and k_2 are reported in Table 2.

Table 2: Parameters for k_1 and k_2 [32].

	A (mol/s.m ² .atm ^{n₀})	E (kJ/mol)
k_1	61	0.5
k_2	20	1074

The oxygen partial pressure at the particle surface ($P_{o_2, s}$) is determined by [32]

$$\frac{P_{o_2, s}}{P} = \left(\frac{P_{o_2, \infty}}{P} - \gamma\right) \exp\left(-\frac{r_c^{\text{Oxid}} d_p}{2C_g D_{O_2, g}}\right) + \gamma, \quad (43)$$

where C_g and $D_{O_2,g}$ are the gas phase concentration and diffusion coefficient of oxygen into the gas phase, respectively. The partial pressure of oxygen at the gas phase represented by $P_{O_2,\infty}$ and $\gamma = (\psi-1)/2$. The value of ψ represents the moles of CO_2 formed per moles of carbon that react,

$$\psi = \frac{CO_2/CO}{1 + CO_2/CO}. \quad (44)$$

CO_2 and CO are the products of char oxidation and there are several models for the ratio of CO_2/CO production. This ratio has a significant influence on the particle temperature that affects the whole coal combustion process [33]. There are several models describing the CO_2/CO ratio [33–35]. In this work, a model from Tognotti *et. al.* is used [35],

$$\frac{CO_2}{CO} = AP_{O_2,s}^{n_r} \exp\left(\frac{B}{T_p}\right), \quad (45)$$

where $A = 0.02$, $B = 3070$ K, $n_r = 0.21$ and $P_{O_2,s}$ is the partial pressure of oxygen at the particle surface (in atm).

To couple the char oxidation model to the gas phase, species source terms appearing in (5) are given in terms of (41) as

$$(S_{p,CO_2})^{Oxid} = \left(\frac{dm_c}{dt}\right)^{Oxid} \psi \frac{M_{CO_2}}{M_c}, \quad (46)$$

$$(S_{p,CO})^{Oxid} = \left(\frac{dm_c}{dt}\right)^{Oxid} (1 - \psi) \frac{M_{CO}}{M_c}, \quad (47)$$

$$(S_{p,O_2})^{Oxid} = -\left(\frac{dm_c}{dt}\right)^{Oxid} \frac{(1 + \psi)}{2} \frac{M_{O_2}}{M_c}. \quad (48)$$

Gasification by H_2O and CO_2 are considered through heterogeneous reactions

with rate constants

$$k_i = A_i P_i^{n_g} \exp\left(-\frac{E_i}{RT_p}\right), \quad i = CO_2, H_2O, \quad (51)$$

where P_i is the partial pressure of CO_2 and H_2O around the particle in (49) and (50), respectively. The rate parameters appearing in (51) are given by [36–38]. In summary, we can write the char gasification term

appearing in (40) as

$$\left(\frac{dm_c}{dt}\right)^{\text{Gasif}} = -(k_{\text{CO}} + k_{\text{H}_2\text{O}}) m_c, \quad (52)$$

where k_{CO} and $k_{\text{H}_2\text{O}}$ are given in (51). The gasification model couples to the gas phase species equations (5) through

$$(S_{\text{p,CO}})^{\text{Gasif}} = \left(2k_{\text{CO}_2} + k_{\text{H}_2\text{O}}\right) m_c \frac{M_{\text{CO}}}{M_c}, \quad (53)$$

$$(S_{\text{p,H}_2})^{\text{Gasif}} = k_{\text{H}_2\text{O}} m_c \frac{M_{\text{CO}}}{M_c}, \quad (54)$$

$$(S_{\text{p,CO}_2})^{\text{Gasif}} = -k_{\text{CO}_2} m_c \frac{M_{\text{CO}_2}}{M_c}, \quad (55)$$

$$(S_{\text{p,H}_2\text{O}})^{\text{Gasif}} = -k_{\text{H}_2\text{O}} m_c \frac{M_{\text{H}_2\text{O}}}{M_c}. \quad (56)$$

Finally, the evolution of particle surface area is accounted using a modified random pore model [39, 40].

2.4 Source terms

The source terms in equations (1)-(5) and (11)-(13) are explained here. To define source terms coupling the gas (intensive properties) and particles (extensive properties), a volume must be defined on each discrete segment of the ODT line. In this work, the effective 3D volume of the discrete 1D line segment is modeled as

$$V_{\text{cell}} = \Delta y A_{\text{cell}} = \Delta y D_j d_p, \quad (57)$$

where Δy is the ODT grid spacing, A_{cell} is the streamwise area of the cell, D_j is the diameter of the jet and d_p is a characteristic particle diameter.

The mass and momentum exchange terms appearing in (1)-(3) are

$$\begin{aligned} S_{pm} &= V_{\text{cell}}^{-1} \frac{dm_p}{dt}, \\ S_{p\vec{u}_i} &= -\frac{m_p f_d}{\tau_p V_{\text{cell}}} (\vec{u}_i - \vec{u}_{p,i}), \end{aligned} \quad (58)$$

where i is the velocity direction, τ_p is the particle relaxation time [41] and f_d is the drag coefficient (see [21] for details).

Given a choice of a devolatilization model to provide $\left(\frac{dm_i}{dt}\right)^{\text{Dev}}$, the species mass source term appearing in (5) is

$$S_{pY_i} = (S_{pY_i})^{\text{Evap}} + (S_{pY_i})^{\text{Dev}} + (S_{pY_i})^{\text{Oxid}} + (S_{pY_i})^{\text{Gasif}}, \quad (59)$$

where $(S_{pY_i})^{\text{Evap}}$, $(S_{pY_i})^{\text{Dev}}$, $(S_{pY_i})^{\text{Oxid}}$ and $(S_{pY_i})^{\text{Gasif}}$ represent species source terms for evaporation (20), devolatilization ((29)-(31) or (38)), char oxidation ((46)-(48)) and gasification ((53)-(56)), respectively.

The energy phase-exchange term in (4) is given in terms of (41) and (52) as

$$\begin{aligned} S_{pe_0} &= \alpha \sum_{i=\text{CO}, \text{CO}_2} (S_{p,i})^{\text{Oxid}} \Delta H_i^{\text{Oxid}} \\ &+ \alpha \sum_{i=\text{CO}, \text{H}_2\text{O}} (-k_i m_c \Delta H_i^{\text{Gasif}}) \end{aligned} \quad (60)$$

where ΔH_i is the enthalpy of (heterogeneous) reaction i , α is percentage of energy that released to the gas and $1 - \alpha$ is the percentage of energy absorbed by the particle. The corresponding energy exchange term for the particle temperature equation, (13), is given in terms of (19), (41) and (52) as

$$\begin{aligned} S_{p,T} &= \frac{1 - \alpha}{m_p C_p} \sum_{i=\text{CO}, \text{CO}_2} (S_{p,i})^{\text{Oxid}} \Delta H_i^{\text{Oxid}} \\ &+ \frac{1 - \alpha}{m_p C_p} \sum_{i=\text{CO}, \text{H}_2\text{O}} (-k_i m_c \Delta H_i^{\text{Gasif}}) \\ &+ \frac{1}{m_p C_p} (S_{p,\text{H}_2\text{O}})^{\text{Evap}} \lambda_{\text{Evap}}, \end{aligned} \quad (61)$$

where λ_{Evap} is the latent heat of vaporization for water.

3 Experimental & Computational Configuration

In this work, an Oxy-Fuel Combustor (OFC) located at the University of Utah is simulated [23, 24]. We choose this experimental dataset because the characterization of flame stand-off distance in this experiment is a good way to measure the coupling between devolatilization and gas phase chemistry which control ignition delay. The OFC is a down-fired configuration with simple primary and secondary jets and optical access across the burner zone. The burner consists of primary stream with 15.8 mm inner diameter and 21.3 mm outer diameter and a secondary stream with 35.05 mm inner diameter. The velocity, temperature and composition of primary, secondary, and effluent (product) streams are reported in Table 3. Further details of the OFC are reported in [23].

Illinois #6 coal with mass-mean size of 68.5 μm and a density of 1450 kg/m³ was fed through the primary stream. The coal is injected in the primary stream at a rate of 5.26 kg/hr and is assumed to be at the velocity and temperature of the carrier gas. In the simulation, particle sizes are assumed to be uniform and equal to

the experimental mass-mean size of $68.5 \mu\text{m}$. The number of particles in the simulation is determined as [21]

$$n_p = \frac{\dot{m}_c d_p}{m_p u_p} \quad (62)$$

where $\dot{m}_c$ is coal flow rate and m_p , d_p , u_p are the particle mass, diameter (assumed to be spherical), and velocity, respectively. An important parameter in the ODT model is the eddy rate constant (C), which has a direct influence on the eddy rate and subsequent mixing intensity. We use $C = 10$ as suggested by [16] for $\text{Re} > 9000$. The impact of C on flame stand-off for this dataset has been studied in [21].

Table 3: Velocity, temperature and composition of burner streams and products.

	u	T	O ₂	CO ₂	H ₂ O
	(m/s)	(K)	volume fraction		
Primary	6.38	305	0.0	1.0	0.0
Secondary	14.92	489	0.488	0.512	0.0
Effluent	0.0	1283	0.048	0.815	0.137

Figure 2: Initial temperature and velocity of ODT line

Figure 2 illustrates the initial temperature and velocity profiles for the ODT simulation. Because ODT cannot capture recirculation, the initial profiles outside of the jet are assumed to be at the effluent conditions. Temporal and spatial resolutions are 200 ns and $200 \mu\text{m}$, respectively, and the results presented here are grid-converged. The nominal “wall-temperature” reported by the experiment is 1280 K; however, in this work 1280 K (nominal wall-temperature), 1600 K and 1800 K are assumed for the effective radiative temperature (T_r in (13)), based on previous work which considered the effect of T_r [21].

Table 4 summarizes the studies considered here. To obtain reasonable statistics, 300 realizations are performed for each case in Table 4.

Table 4: Parameters for simulations considered herein.

Case no	Devolatilization Model	Gas Chemistry Model	T_r (K)
A.1	CPD	detailed	1280
A.2	CPD	detailed	1600
A.3	CPD	detailed	1800
A.4	Two-Step	detailed	1600
B.1	CPD	flame-sheet	1280
B.2	CPD	flame-sheet	1600
B.3	CPD	flame-sheet	1800
B.4	Two-Step	flame-sheet	1600

The flame stand-off measured by the experiment is used as the metric for comparing the devolatilization and gas-phase kinetics models considered here. The methodology for characterizing flame stand-off is reported in [22,23], and the computational analog has been described in [21]. Applying this to the 300 ODT realizations, a PDF of the flame stand-off distance is obtained for each case in Table 4.

4 Results & Discussion

This section presents the results from the simulations described in §3 and summarized in Table 4.

4.1 Influence of Gas Phase Kinetics Models

We first consider the influence of gas-phase kinetics modeling by comparing results from the flame-sheet and detailed kinetics models.

Figure 3 shows the contour plots of gas phase temperature, O_2 and CO_2 mass fractions and equivalence ratio (Φ) using detailed kinetics (case A.2, depicted on the left half-plane) and flame-sheet (case B.2, depicted on the right half-plane) models. These are generated by ensemble averaging over 300 realizations to produce adequate statistics, and both cases employ the CPD model for devolatilization.

At $\ell \approx 0.25$ m the coal particles start to release volatiles (as will be shown quantitatively in Figure 7b). For the flame-sheet model, this results in an immediate increase in temperature and consumption of available

Figure 3: Gas properties predicted using detailed kinetics (DK) and flame-sheet (FS) models paired with the CPD devolatilization model (case A.2 & B.2).

oxidizer as devolatilization proceeds. This, in turn, increases the particles' temperature and accelerates the devolatilization process.

In the detailed kinetics calculation, the homogenous oxidation of volatiles is slow due to the relatively low temperature of the gas phase. Consequently, there is a notable delay in oxygen consumption and temperature rise relative to the results from the flame-sheet model. For both models, the CO₂ decreases due to dilution by volatiles. However, there is a notable difference in the structure of the flame as indicated by the gas phase temperature, which is much more structured for the flame-sheet model than for detailed kinetics. This is primarily because the detailed kinetics model allows more time for mixing to provide a more homogeneous mixture than the flame-sheet model, where the reaction zone is dictated only by stoichiometry. This is further substantiated by Figure 3d, which indicates a much more pronounced transition in equivalence ratio for the flame-sheet model than for the detailed kinetics model.

Figure 4 shows the predicted flame stand-off distance probability distribution function (PDF) for both gas-phase chemistry models (cases A.1, A.2, A.3, B.1, B.2 and B.3) as well as the experimentally-observed flame stand-off for a range of effective radiative temperatures. Figure 4 indicates that:

1. The flame-sheet model predicts a shorter *mean* flame stand-off distance than the detailed kinetics

Figure 4: Flame stand-off distance PDF using detailed kinetic (DK) and flame-sheet (FS) models at given radiative temperature (Cases A.1, A.2, A.3, B.1, B.2 and B.3). Blue circles are the characterized minimum flame stand-off distance for the given radiative temperature.

model.

2. The flame stand-off PDF in the flame-sheet model is narrower than in the detailed kinetics model.
3. The *minimum* flame stand-off distance is not sensitive to the gas-phase chemistry model.

The flame stand-off distance is influenced by the rate of devolatilization (CPD was used for all cases in Figure 4) as well as the gas-phase kinetics. As discussed previously in connection with Figure 3, the flame-sheet model has a strong thermal feedback to the particles at the onset of devolatilization, which increases the devolatilization rate. This is clearly observed in Figure 4, where the flame stand-off PDF is narrower for the flame-sheet model. Given the significant difference in mean flame stand-off, it is clear that the finite-rate chemistry model has an appreciable effect. The nonlinear feedback mechanism between gas-phase chemistry (heat release) and devolatilization makes the flame stand-off particularly sensitive to the gas-phase chemistry model.

Interestingly, the minimum flame stand-off is insensitive to the gas-phase kinetics model, suggesting that minimum flame stand-off is controlled solely by devolatilization rates prior to ignition, which are, in turn, governed by convective and radiative heat transfer alone. Thus, minimum flame stand-off is governed by heat transfer to particles from the (non-reacting) environment while the width of the flame stand-off PDF is influenced significantly by the gas-phase kinetics model. Previous work by the authors [21] showed that the minimum flame stand-off distance is insensitive to the mixing rate, and showed that there is a minimum devolatilization threshold required to achieve ignition.

Given that the effective radiative temperature of 1600 K yields results that are closest to the experimental data in Figure 4, we use this for the remainder of the results presented in this paper.

Figure 5 shows the mean particle temperature and mass evolution, with the range (maximum/minimum) indicated by vertical bars. The solid and dotted lines indicate the detailed kinetics (DK) and flame-sheet (FS) models in the gas phase, respectively. As previously mentioned, the flame-sheet model results in a more rapid particle heat-up, and a correspondingly reduced devolatilization time period. Note that the onset of devolatilization is the same in both cases (deviating only after $\sim 10\%$ of the volatiles are liberated), which is the minimum devolatilization required to achieve ignition under these conditions [21].

Figure 5: Results for Cases A.2 & B.2 showing the impact of the gas chemistry model on particle behavior: (a) particle temperature (b) normalized volatile and char mass. Vertical bars indicate the range of values observed while lines indicate the mean value across all particles at that downstream location.

Char consumption is active at $\ell \gtrsim 0.35$ m and, as shown previously, both gasification and oxidation processes are active during the early stages [21] due to the rich environment created by the volatile cloud and diffusion of products of combustion (CO_2 and H_2O) back to the coal surface. However, due to the different particles' temperatures, the rate of char consumption for the flame-sheet model is higher than the detailed kinetics. After devolatilization is nearly complete, however, both gas-phase kinetics models show the same rate of char oxidation (slope of $\langle m_c \rangle$), which is essentially diffusion-limited by oxidizing/gasifying species to the particle. In summary, the detailed kinetics model can have an appreciable effect on the duration of devolatilization, which has important implications for prediction of flame stand-off distances. This is primarily because of the different thermal time-histories that particles are subjected to with flame-sheet versus detailed kinetics models in the gas phase.

4.2 Influence of Coal Devolatilization Models

This section explores the impact of the level of modeling used for the devolatilization process. We consider the two-step (TS) and CPD models, as described in §2.3.

The devolatilization model has a notable impact on the flame stand-off shape and minimum as illustrated in Figure 6, which shows the flame stand-off PDF for each of the devolatilization models paired with detailed kinetics (DK) and flame-sheet chemistry (FS) in the gas phase. The shape of the PDF is very similar for the TS and CPD models, but using the flame-sheet model has a more pronounced effect on the mean flame stand-off for the TS model than CPD. Interestingly, the TS model paired with the flame-sheet model results in compensating errors: the delay in TS devolatilization is compensated by the flame-sheet nonlinear feedback discussed in §4.1. Furthermore, the CPD model is not as sensitive to changes in the gas phase model as the TS model.

Figure 6: Flame stand-off PDFs for cases A.2, A.4, B.2 & B.4.

The discrepancy in prediction of flame stand-off distance using CPD and TS models decreases when employing flame-sheet rather than detailed kinetics calculation. The flame-sheet model eliminates the impact of volatile composition and highlights the influence of volatile yield on flame stand-off prediction. Therefore, the slight discrepancy between devolatilization models in prediction of flame stand-off distance using flame-sheet model can be attributed to the difference in volatile yield in each model.

Figure 7 shows the histories for particle volatile content (Figure 7b) and temperature (Figure 7a) as well as the range of values (vertical lines). The TS model shows a more rapid devolatilization with an onset slightly delayed relative to CPD. These slight differences in devolatilization onset have significant implication for flame stand-off and, therefore, particle temperature histories, shown in Figure 7a. The other noteworthy difference between these models is the yield, which is higher for TS than CPD, and results in higher particle temperatures. Note that char oxidation does not play a major role until further downstream [21].

Figure 7: Particle behavior with various devolatilization models for cases A.2 & A.4. All cases use detailed kinetics in the gas phase.

The cost of each model pairing is quite dependent on number of particles relative to number of gas phase cells, the particular gas-phase chemical mechanism, *etc.* For the cases considered here, the simulation is 3-4 times faster when using the flame-sheet than detailed kinetics. The CPD model involves many more ordinary differential equations than the two-step model, which makes this model an order of magnitude more expensive to calculate than the two-step model. In the situation here, this had little impact on the overall simulation cost due to the relatively low number of particles considered.

5 Conclusions

The oxy-coal combustion process is simulated using different levels of modeling in the gas and the coal particle phases through the ODT model. The flame stand-off predicted by simulation is compared with experimental data. Significant sensitivity to the level of modeling for gas phase kinetics as well as devolatilization was observed. It was shown that the minimum flame stand-off distance is insensitive to the gas phase chemistry model, but quite sensitive to the devolatilization model (and system parameters such as radiative temperature that affect devolatilization). It suggests that minimum flame stand-off distance is controlled by devolatilization rate prior to ignition. It was shown that the detailed kinetic model have a considerable impact on the duration of devolatilization. Furthermore, the TS model shows a more rapid devolatilization, however, slightly delayed relative to the CPD model. The yield is higher in TS than CPD model, and results in higher particle temperature. Finally, pairing the simple two-step devolatilization model and the simple flame-sheet chemistry model had competing errors that resulted in a relatively good representation of the flame stand-off PDF. Further research is needed to determine how universal these conclusions

are with respect to system variation, coal type variation, *etc.* However, the ODT model presented here is a cost-effective means to evaluate the adequacy of various model pairings for use in more expensive LES calculations.

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