Kinetic modeling of the formation and growth of inorganic nano-particles during pulverized coal char
combustion in O₂/N₂ and O₂/CO₂ atmospheres

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Abstract: In the formation of nano-particles during coal char combustion, the vaporization of inorganic components in char and the subsequent homogeneous particle nucleation, heterogeneous condensation, coagulation, and coalescence play decisive roles. However, conventional measurements cannot provide detailed information on the dynamics of nano-particle formation and evolution. In this work, a sophisticated intrinsic char kinetics model that considers ash effects (including ash film formation, ash dilution, and ash vaporization acting in tandem), both oxidation and gasification by CO₂ and H₂O, homogeneous particle nucleation, heterogeneous vapor condensation, coagulation, and coalescence mechanisms is developed and used to compare the temporal evolution of the number and size of nano-particles during coal char particle combustion as a function of char particle size, ash content, and oxygen content in O₂/N₂ and O₂/CO₂ atmospheres. Based on comparisons with measurements of char particle temperature, carbon conversion, mineral vaporization, and mean size of nano-particles at various residence times, the model can accurately predict the transient combustion of pulverized coal char particles and nano-particle formation and growth. Model results show that in either O₂/N₂ or O₂/CO₂ atmospheres, the char combustion temperature has a dominant effect on the formation and

growth of nano-particles. High char burning temperatures result in a high mineral vaporization rate within the char particle, and subsequent high nucleation and condensation rate, and consequently more and larger nano-particles. As a result, high oxygen content, low ash content, and small sized char particles, all of which promotes high local char burning temperatures, yield more nano-particles and shift the nano-particle size distribution to larger sizes. In comparison to combustion in O_2/N_2 , both the number density and size of the nano-particles formed in O_2/CO_2 are lower. Unlike condensation, which contributes to particle growth until the vapor molecules are fully consumed, nucleation ceases during the last stage of char combustion.

Keywords: coal char combustion; nano-particle; vaporization; nucleation; condensation; coalescence; kinetic model; O_2/N_2 ; O_2/CO_2

Nomenclature:

Symbols			
A	pre-exponential factor (kg/s/cm ² /atm ⁿ)	N	particle number concentration (N/cm ³)
A_c	pre-exponential factor for CO/CO ₂ product ratio, 50	N_A	Avogadro's number
c	vapor concentration in char (mol/m ³)	n_c	oxygen exponent for CO/CO ₂ product ratio, 0.21
d, d'	diameter (cm)	N_m	number of inclusions
D	diffusion coefficient (cm ² /s)	q	burning rate (g/cm ² /s)
E	activation energy (kJ/mol)	P	pressure (atm, Pa)
E_c	activation energy for CO/CO ₂ product ratio, 3070	r	radius (cm)
f	number fraction	$\bar{r}$	average radius of the pore channel (cm)
F	mass fraction	R	ideal gas constant (8.314 J/mol/K)
FCO_2	fraction of CO ₂	S	extent of saturation
I	rate of nucleation (N/cm ³ /s)	S_g	internal specific surface area (cm ² /g _C)
k_B	Boltzmann constant, 1.38×10 ⁻²³ J/K	T	temperature (K)
K	cohesion factor (cm ³ /s)	V	volume (cm ³ /s)
m	molecular mass (g)		vaporization rate (mol/s)
M	molar mass (g/mol)	X	mole fraction of vapor at the inclusion surface
MO_n	metal oxides	Y	ash content
MO_{n-1}	metal suboxides and metals	ΔG_v	change in Gibbs' free energy for droplet formation per unit volume
Greek alphabet			
α	Stefan flow factor	Φ	Thiele modulus
α_c	condensation coefficient	ν	molecular volume (cm ³)
α_m	activity of metal oxides	τ	tortuosity
ρ	mass density (g/cm ³)	σ	surface tension of liquid
η, η'	effectiveness factor	σ_c	constriction factor
θ	porosity	σ_{MO-N_2}	collision cross section for vapor and nitrogen molecules
θ'	volume fraction of inclusion in char	λ	mean free path of gas molecules
Subscript			
0	initial	g	bulk gas
a	ash	j,i	serial numbers of different sized particles
a,f	porous ash	int	intrinsic
b	burnout	M	metal sub-oxide or metal
c	carbon	MO	metal oxide or inclusion
cc	char core	O ₂	molecular oxygen

cs	char core surface	rxn	reaction
crit	critical	s	surface
eff	effective	tot	total
eq	equilibrium		
Superscript			
eq	equilibrium	s	surface
<i>n</i>	reaction order		

1. Introduction

Submicrometer particles (smaller than 1.0 μm in aerodynamic diameter) generated during pulverized coal combustion are difficult to capture and can penetrate deeply into the lungs and consequently cause various diseases, particularly because they may contain a variety of trace toxic compounds [1-4]. Coal combustion has been recognized as a major source of fine particles in the environment in many places throughout the world. The mass size distribution of fine particles produced from coal combustion shows a bimodal or trimodal character [3-11]. In these particle size distributions there is a peak in the range of 0.05–0.3 μm referred to as the ultrafine mode [3, 10-12]. In comparison with the coarse mode, ranging from several to tens of micrometers [10-12], and the fine-fragment mode, located between a half and several micrometers [3, 10], ultrafine particles are difficult to remove with conventional particulate control devices. Consequently, although ultrafine particles account for only 0.2–2.2 percent of the total fly ash mass during coal combustion in boilers, they make up nearly all of the particles that discharge into the atmosphere [5].

Within the large body of literature on the possible pathways of fine particle formation in coal combustion, Tian et al. [10] and Wen et al. [11] recently summarized the current state of knowledge, wherein fine particles can form from 1) the release of organically bound metals during coal devolatilization, 2) the vaporization and subsequent condensation and aggregation of inorganic elements, 3) direct transformation of fine mineral grains, 4) both char and excluded mineral fragmentation, 5) included mineral coalescence, 6) surface ash shedding during char combustion, 7) bursting of cenospheres, and 8) agglomeration of molten minerals. It is commonly understood that the direct transformation of fine mineral grains, molten ash accumulation, and the fragmentation of char particles and excluded minerals (mechanisms 3-8) dominate the formation of coarse mode and fine-fragment mode particles. The continuous vaporization of inorganic components in char, and subsequent homogeneous nucleation, heterogeneous condensation, coagulation, and coalescence (mechanisms 1 and 2) play dominant roles in the formation of ultrafine particles (i.e. nano-particles) [4, 13]. During char combustion, alkali and alkali-earth elements (e.g., K, Na, Mg, and Ca)

exist in both internal and external minerals, refractory elements (e.g., Si, Al, and Fe) mainly exist in external minerals, and volatile trace elements (e.g., Hg, As, and Se) mainly exist as organic constituents or elementary substances that vaporize and diffuse out of the char first. Then, as the concentration of the vaporized molecule increases, the volatile components participate in particle nucleation, vapor condensation, coagulation, and coalescence to form submicron-sized particles [4, 14, 15]. However, in comparisons with refractory elements and alkali-earth elements, the trace elements are very little, and consequently the effect on nano-particles can be ignored.

Additional studies have indicated that combustion temperature and the gaseous atmosphere affect the formation of nano-particles [3, 4, 6, 12, 16, 17], with an increased temperature leading to increased mineral vaporization, condensation, and subsequent coagulation and coalescence [4, 6], whereas a low oxygen-to-fuel stoichiometry lowers the fraction of ultrafine ash [3]. Meanwhile, a drop tube study found that in comparison with traditional combustion in air (O_2/N_2), oxy-fuel combustion (O_2/CO_2) did not significantly affect the overall size distribution of the residual ash particles but markedly altered the size distribution and composition of the submicron particles. In particular, O_2/CO_2 combustion at the same oxygen concentration shifted the submicron mode to smaller particles, at a lower concentration, while increasing the oxygen concentration minimized the difference between the two combustion atmospheres and had a greater impact on the formation of submicron particles in O_2/CO_2 combustion [12].

In addition, coal rank and char properties have a significant impact on the formation of submicrometer particles [4, 11, 17]. Higher char reactivity associated with lower rank coals can enhance the formation of submicrometer particles because of the resultant higher char combustion temperature [11]. Also, the carbon matrix produces a locally reducing atmosphere when reacting at high temperature, which can augment ash vaporization [4]. In addition, the fine distribution of alkaline metals in low-rank coals suppresses SiO_2 vaporization by reacting with the silica to form less volatile silicates [4]. Consequently, submicrometer particles formed during the combustion of lignite are dominated by MgO and CaO, whereas SiO_2 is

predominant for bituminous coal [4, 18].

The understanding of submicron particle formation described above is largely based on the analysis of residual particles formed in experiments.. In the formation of nano-particles, the vaporization of inorganic components in char, subsequent homogeneous nucleation, heterogeneous condensation, coagulation, and coalescence play decisive roles. However, conventional measurement technologies cannot provide direct information about these formation processes. Consequently, kinetic modeling that can reveal the temporal evolution of vapor concentrations and particle size during vaporization, nucleation, condensation, coagulation, and coalescence at different char combustion temperatures in different combustion atmospheres is needed. Previous research has shown that the available surface area, porosity, and ash distribution in char significantly affect the carbon conversion rate and the char particle combustion temperature [19], and consequently the vaporization of inorganic components and formation of nano-particles. In comparison with apparent kinetics char reaction models, which can only describe the overall burning rate of the particle, an intrinsic kinetics approach coupled with models for char parameter changes during burnout is an effective means to model the formation and growth of nano-particles during char combustion.

We previously developed an intrinsic kinetics char combustion model with ash that considers the possibility of an ash film effect, an ash dilution effect, or some arbitrary combination of the two effects acting in tandem [20]. This model has been shown to accurately characterize the impact of ash on the temporal evolution of char combustion during burnout. In the current work, a sophisticated model of the formation and growth of nano-particles during char combustion is developed by considering the thermodynamics and chemical reaction kinetics of inorganic ash components (vaporization submodel), nucleation theory (homogeneous nucleation submodel), and molecular dynamics theory (heterogeneous condensation and coalescence submodels). The effects of the surrounding oxygen content, char particle size, and ash content (factors with a significant influence on char conversion during combustion) are analyzed on the basis of the newly developed model in both O_2/N_2 (conventional) and O_2/CO_2 (oxy-fuel) atmospheres.

2. Model descriptions

2.1 Description of the intrinsic kinetics model of pulverized coal char combustion

Fig.1 Schematic of integrated ash film and ash dilution model (black-and-white in print, and color on Web)

A detailed description and verification of our intrinsic kinetics ash inhibition model of pulverized coal char combustion has been presented previously [20]. An overview of this model is provided with reference to a schematic of the model shown in Fig.1. As the char temperature increases, the char combustion first undergoes chemical reaction control (Zone I), during which the char density decreases, but its size remains unchanged. Eventually, the char surface reaction rate exceeds the ability of O_2 diffusion to maintain the O_2 concentration at the center of the particle, so it reacts under the combined control of chemical reaction and oxygen diffusion (Zone II), during which both char particle density and size decrease. Finally, at even higher temperatures, the reaction rate becomes so large that all of the O_2 diffusing to the particle is consumed on the external char surface, such that the particle reacts under full oxygen diffusion control (Zone III), during which the char density is constant, but its size decreases.

In the model the initial char particle is divided into a number of equally spaced concentric shells, and during combustion the particle is idealized as consisting of an external ash film and an internal char core where ash and pore are distributed into the carbon matrix uniformly. It is assumed that some fraction of the ash components liberated during combustion of each burned shell is used to thicken the ash film, and the rest is assumed to penetrate and be uniformly distributed in the char core, an effect that has some degree of experimental support [21]. The effect of the small component of ash that typically vaporizes and is responsible for the formation of nano-particles on combustion is ignored, at least with respect to char combustion. The reacting char particle is assumed to be spherical and to have uniform properties throughout.

Oxidation and both CO₂ and steam gasification reactions, as listed below, are included in the model. Following the recommendations of Hecht et al. [22, 23], the activation energy is set as 150 kJ/mol for oxidation (R1), 251 kJ/mol for gasification by CO₂ (R2), and 222 kJ/mol for gasification by H₂O (R3). On the basis of the authors' previous study [20], the intrinsic reaction orders for oxidation and gasification reactions are assumed to be 0.1 and 0.5, respectively, and the pre-exponential for char oxidation is set to 8.0 kg/s/cm²/atm^{0.1}. The pre-exponentials for the gasification reactions are selected by comparing both the char particle combustion temperature and the carbon conversion between model predictions and benchmark experimental measurements, as described later.

Considering the effect of internal reaction in the char particle, as characterized by the effectiveness factor η , the ash distribution $Y_{a,cc}$, and the porosity θ , the gross carbon conversion rate, q_{tot} , is calculated according to Eq.1.

$$q_{tot} = (1 - Y_{a,cc} - \theta_{c,cc} + \frac{\eta \rho_{c,cc} S_g d_{cc}}{6}) (q_{O_2,int} + q_{H_2O,int} + q_{CO_2,int}) \quad (Eq. 1)$$

where the burning rate of pure carbon through the oxidation reaction R1, $q_{O_2,int}$, is calculated according to the Arrhenius expression shown in Eq. 2. Both $q_{H_2O,int}$ and $q_{CO_2,int}$ have similar expressions.

$$q_{c,int} = A_{int} \exp(-E_{int}/RT_{cc}) P_{O_2,cc}^{n_{int}} \quad (Eq. 2)$$

Considering the changes of carbon content, ash content, and porosity during burnout, the effective diffusion coefficient in the porous char particle, D_{eff} , is proposed to follow Eq. 3 [20]. D is the molecular diffusivity of reactants and is calculated according to the approach presented by Paul and Warnatz [24]. σ_c is

the constriction factor, τ is the tortuosity, and τ/σ_c is assumed to be 6.0 [25].

$$D_{eff} = \frac{D \sigma_c}{\tau} \left(\frac{\theta_{a,f} V_{a,cc}}{V_{cc}} + \frac{\theta_c V_{c,cc}}{V_{cc}} \right) \quad (\text{Eq. 3})$$

2.2 Descriptions on the model of formation and growth of nano-particles

Inorganic components in coal mainly exist in the form of oxides such as SiO_2 , Al_2O_3 , FeO , CaO , MgO , K_2O , and Na_2O , and minerals such as kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), siderite (FeCO_3), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). During char combustion, the minerals decompose into oxides at high temperatures. Thus, the primary assumptions in the model are as follows:

- 1) All minerals are uniformly distributed as oxide inclusions throughout the char particle and vaporize in the form of sub-oxides or fully reduced metals.
- 2) The spherical inclusions are much smaller than the char particle, and each kind of inclusion is specified to have a single size.
- 3) The nano-particles result from mineral vaporization and contain all the vaporized materials, i.e., no nano-particles are modeled as forming from char fragmentation.
- 4) Vaporization is driven by the vapor concentration of sub-oxides or metal atoms at the inclusion surface.
- 5) Vaporization is limited by the diffusion of volatile species from the inclusion surface to the char surface. Diffusion of volatile species through the porous char matrix and the external ash film is their primary flow resistance. The re-oxidization of sub-oxides and metal is very fast, and the reaction time can be ignored.
- 6) Homogeneous particle nucleation and heterogeneous condensation and coagulation of nano-particles are modeled simultaneously during combustion; coalescence is calculated post-flame, after the formation of the nano-particles.

Based on the above hypotheses, the model is divided into four submodels including the mineral

vaporization submodel, the homogeneous nucleation submodel, the heterogeneous condensation submodel, and the coalescence submodel.

2.2.1 Vaporization submodel

The bulk ash is composed of refractory metal oxides (SiO_2 , Al_2O_3 , CaO , MgO , and FeO) that have relatively low oxide vapor pressures and do not volatilize appreciably as oxides at typical combustion temperatures. However, when the char particle combustion temperature is above 1800 K, the carbon oxidation rate is sufficiently fast that the oxygen partial pressure within the porous char is extremely low, and the local reducing environment may facilitate the chemical reduction of refractory metal oxides to highly volatile suboxides (SiO and Al_2O) and metals (Mg , Ca , and Fe) by heterogeneous reaction R4 [26].

where MO_n represents refractory oxides, and MO_{n-1} represents sub-oxides and metals.

When reaction R4 reaches equilibrium at the surface of each inclusion within the char particle, the partial pressure of the suboxide and metal, P_M^{eq} , at the surface of each inclusion can be determined from the reaction equilibrium constant, K_{eq} , and the local CO and CO_2 partial pressures, as shown in Eq. 4.

$$P_M^{\text{eq}} = K_{\text{eq}} \frac{\alpha_{\text{MO}} P_{\text{CO}}}{P_{\text{CO}_2}} \quad (\text{Eq. 4})$$

where α_m is the activity of the metal oxides in the inclusion. The metal oxide activity is here simply taken as 1.0, though it should be less than 1.0 and should vary with different fuels, ash components, and combustion conditions because of the interaction of ash components. K_{eq} can be calculated according to the NASA thermodynamic database or the NSRDS-JANAF Thermochemical Tables [27]. For $P_{\text{CO}}/P_{\text{CO}_2}$, the simple Arrhenius power-law expression, $\text{CO}/\text{CO}_2 = A_c \exp\left(\frac{E_c}{T_{\text{cc}}}\right) P_{\text{O}_2}^{-n_c}$, proposed by Hurt et al. for the product composition of char combustion is adopted [28].

Based on the diffusion rate of vapor within the porous char, the total vaporization rate of isolated

inclusions, V , is given by Eq. 5.

$$V = N_{\text{MO}} 4\pi r_{\text{MO}} c D_{\text{eff}}' X_{\text{M}}^{\text{eq}} \quad (\text{Eq. 5})$$

where c is the vapor concentration in the char particle, D_{eff}' is the effective Kundsens diffusivity in the porous char, r_{MO} is the inclusion radius, X_{M}^{eq} is the equilibrium mole fraction of the vapor at the inclusion surface, and N_{MO} is the number of inclusions. N_{MO} employed in current model is a function of transient char particle size r_{cc} and the volume fraction of inclusions in the char θ' , and is given by Eq. 6. Alternatively, Quann and Sarofim [26] adopted Eq. 7 to calculate N_{MO} . During char combustion, char temperature, available surface, and porosity continuously change, and consequently the carbon burning rate changes. Thus, the square of char particle size does not obey the straight-line d^2 -law relative to time. However, the d^2 -law is appropriate during zone III combustion, where a pure shrinkage model is appropriate. It should be noted that because of the ash dilution effect and mineral vaporization, θ' , as calculated according to Eq. 8, is a variable.

$$N_{\text{MO}} = \theta' \left(\frac{r_{\text{cc}}}{r_{\text{MO}}} \right)^3 \quad (\text{Eq. 6})$$

$$\text{or } N_{\text{MO}} = \theta' \left(\frac{r_0}{r_{\text{MO}}} \right)^3 \left(1 - \frac{t}{t_b} \right)^{3/2} \quad (\text{Eq. 7})$$

$$\theta' = \frac{6(F_{\text{MO}} m_{a,cc} - m_{\text{vap}})}{\rho_{\text{MO}} \pi d_{\text{cc}}^3} \quad (\text{Eq. 8})$$

According to the ideal gas law, the total mineral vaporization rate, V_{tot} , can be given by Eq. 9. The effectiveness factor, η' , given by Eq. 10, is the ratio of the total vaporization rate of inclusions within the particle, as moderated by ash interactions and vapor diffusion rates, divided by the vaporization rate of N_{MO} isolated inclusions within the char. The Thiele modulus Φ and the effective diffusion coefficient D_{eff}' are calculated according to Eq. 11 and Eq. 12, respectively. In practice, the inclusion size, r_{MO} , varies with char burnout because of vaporization and the merging of molten inclusions, while also depending on coal type [29].

$$V = \eta' N_{\text{MO}} 4\pi r_{\text{MO}} D'_{\text{eff}} \frac{P_{\text{M}}^{\text{eq}}}{RT} \quad (\text{Eq. 9})$$

$$\eta' = \frac{3}{\Phi} \left(\frac{1}{\tanh \Phi} - \frac{1}{\Phi} \right) \left[1 + \frac{D'_{\text{eff}}}{\alpha D_{\text{O}_2}} \left(\frac{\Phi}{\tanh \Phi} - 1 \right) \right]^{-1} \quad (\text{Eq. 10})$$

$$\Phi = (3\theta')^{0.5} \frac{r_{\text{cc}}}{r_{\text{MO}}} \quad (\text{Eq. 11})$$

$$\begin{aligned} D'_{\text{eff}} &= \frac{D_{\text{M}} \sigma_c}{\tau} \left(\frac{\theta_{a,f} V_{a,cc}}{V_{\text{cc}}} + \frac{\theta_c V_{c,cc}}{V_{\text{cc}}} \right) \\ &= 9700 r_{\text{M}}^{-1} \frac{T_{\text{cc}}}{M_{\text{M}}} \frac{\sigma_c}{\tau} \left(\frac{\theta_{a,f} V_{a,cc}}{V_{\text{cc}}} + \frac{\theta_c V_{c,cc}}{V_{\text{cc}}} \right) \end{aligned} \quad (\text{Eq. 12})$$

2.2.2 Homogeneous nucleation submodel

According to the classical nucleation theory developed by Volmer, Weber, Becker, and Doring [17, 18, 30], the rate of nucleation, I , given by Eq. 13, is governed by the net number of clusters per unit time which grow larger than the critical cluster size, d_{crit} (Eq. 14). Any cluster which fluctuates to a size larger than the critical size will probably grow to macroscopic size while clusters smaller than the critical size will most likely shrink back to being monomers. Thus, when the cluster grows to the critical size, addition of one more vapor molecule will promote the nucleation. P_{MO}^s is the sum of the partial pressures attributed to the remaining vapor molecules after homogeneous nucleation and heterogeneous condensation during the previous time step plus the newly generated vapor molecules originating from vaporization-reoxidation reactions. In comparison with the proposal of Neville et al. [4] that nano-particles are formed through one-time nucleation at the beginning with subsequent simple condensation, transient nucleation and condensation happen simultaneously over a time-scale as short as 10^{-5} s in the current model. More detailed descriptions of nucleation of inorganic vapor during coal combustion are given by Neville [18].

$$I = \frac{2\alpha_c P_{\text{MO}}^s{}^2 \sigma^{0.5} v_{\text{MO}}}{(2\pi m)^{0.5} (k_B T)^2} \exp\left(\frac{-16\pi\sigma^3}{3k_B T \Delta G_v}\right) \quad (\text{Eq. 13})$$

$$d_{\text{crit}} = \frac{4\sigma v_{\text{MO}}}{k_B T \ln S} \quad (\text{Eq. 14})$$

2.2.3 Heterogeneous condensation submodel

Once nano-particles are formed, their surface area is far greater than that available on the larger, but much less numerous, residual fly-ash particles. Consequently, heterogeneous condensation on the residual ash particles occurs at such a low rate that it is negligible [4, 5]. The newly formed nano-particles will continue to grow through heterogeneous condensation and coagulation. According to the theory of gas molecular dynamics, when the newly formed stable cluster is much smaller than the mean free path of the gas molecule λ (i.e, when the Knudson number, Kn , equal to $2\lambda/d'$, is significantly larger than 1.0) the rate of heterogeneous condensation of vapor molecular on the newly formed stable cluster will be controlled by the frequency with which the vapor molecules collide with the clusters in a random fashion. The rate of condensation per particle of size d' is given by Eq. 15a. $P_{\text{MO}}^{s'}$ is the partial pressure of remaining vapor molecules after nucleation in one transient time step (10^{-5}s) and d' is the newly nucleated particle diameter.

$$n_c = \frac{\pi d'^2 (P_{\text{MO}}^{s'} - P_{\text{MO}}^{eq})}{\sqrt{2\pi m k_B T}} \quad (\text{Eq. 15a})$$

If the mean free path of the gas molecule is much smaller than the nucleated particle (i.e. if Kn is significantly less than 1.0), the continuous growth of the nano-particles will depend on molecular diffusion of vapor to the surface rather than on random collisions. Then the rate of condensation per particle of size d' is equal to Eq. 15b, where the molecular diffusion coefficient D_{MO} is calculated according to Eq. 16. Alternatively, McNallan et al. [17] proposed Eq. 17 to calculate the molecular diffusion coefficient, because of the dominant nitrogen fraction in O_2/N_2 atmospheres.

$$n_c = 2\pi d' D_{\text{MO}} \frac{(P_{\text{MO}}^{s'} - P_{\text{MO}}^{eq})}{k_B T} \quad (\text{Eq. 15b})$$

$$D_{MO} = \left(\frac{8k_B T}{\pi m} \right)^{0.5} \quad (\text{Eq. 16})$$

$$D_{MO} = 0.0018583T^{3/2} (M_{MO} + M_{N2})^{1/2} / P \sigma_{MO-N2}^2 \quad (\text{Eq. 17})$$

In the transition regime (i.e., for Kn approximately equal to 1.0), the rate of condensation per particle of size d' is given by Eq.15c.

$$v = \frac{2\pi d' D_{MO}' (P_{MO} - P_{MO}^{eq})}{k_B T} \frac{1 + Kn}{1 + 1.71Kn + 1.333Kn^2} \quad (\text{Eq. 15c})$$

When $Kn \ll 1$, Eq. 15c reduces to Eq. 15b. Alternatively, when $Kn \gg 1$, Eq. 15c approaches the form of Eq. 15a, given that $D_{MO}' = 1/3 D_{MO}$. Accordingly, the nano-particle size can be calculated on the basis of volume conservation. In this paper, we take Kn of 0.1–10 as the transition boundary.

2.2.4 Coagulation and coalescence submodel

When nano-particles are formed through nucleation and condensation, they may randomly collide and stick together to form larger particles, and consequently their size increases and total number decreases. The collisions of nanoparticles with larger residual fly-ash particles is comparatively small, because of the much lower concentration of fly-ash particles [4]. For monodisperse spherical particles, the collision frequency or the change of particle number concentration can be calculated according to Eq. 17, where K_{coh} is the cohesion factor [31].

$$\begin{aligned} \frac{dN}{dt} &= 4\pi d' D' N^2 \\ &= K_{coh} N^2 \end{aligned} \quad (\text{Eq. 17})$$

Assuming that K_{coh} is constant and the initial particle number concentration is N_0 , then the temporal change of particle number concentration, N , can be given as Eq. 18, after performing time integration on both sides of Eq. 17. Then, the particle size can be calculated according to mass conservation.

$$N = \frac{N_0}{1 + N_0 K_{coh} t} \quad (\text{Eq. 18})$$

Based on the above expressions for a monodisperse system, the particle number concentrations and particle sizes in a polydisperse system of spherical particles can be calculated from the particle number concentrations and size distributions generated from the nucleation and condensation submodels. It is assumed that the different sized particles pairwise collide in proportion to their number fractions first, and then the newly formed particles and the remaining particles that did not participate in the previous round of collisions pairwise collide again in the next time step according to their number fractions. The continued collisions cause the particle size to increase and the number concentration to decrease. The cohesion factors, $K_{i,j}$, for particle collisions involving particles of size i and j is given by Eq. 19.

$$K_{i,j} = \pi(d'_i + d'_j)(D'_i + D'_j) \quad (\text{Eq. 19})$$

The newly formed particle number concentrations $N_{i,j}$, can be calculated by Eq. 20 where f is the number fraction of each type of initial particle. Similarly, the size of newly formed particles can be calculated according to mass conservation.

$$N_{i,j} = \frac{N_i f_j + N_j f_i}{1 + (N_i f_j + N_j f_i) K_{i,j} t} \quad (\text{Eq. 20})$$

3. Results and discussion

3.1 Benchmarks

The char combustion temperature (which determines the reaction equilibrium constant of vaporization), the carbon conversion rate (which affects the reducing atmosphere within the char particle and subsequently mineral vaporization), and the vaporization rate and vaporized fraction of mineral inclusions (influencing particle nucleation, vapor condensation, and consequently particle coalescence and the particle size distribution), are the key rate phenomena controlling the formation and growth of nano-particles. Consequently, when modeling nano-particle formation it is important to evaluate the modeling precision for char combustion temperature, carbon conversion ratio (or carbon conversion rate), and mineral vaporization rate. The newly developed model's predictions of these aspects of char combustion, as well as the evolution

of nano-particle size with residence time, are therefore compared with benchmark experimental data. Unfortunately, the available data for nano-particle evolution with residence time are limited to raw coal combustion. Therefore, the expected minor contribution of atomically dispersed mineral release during coal devolatilization to nano-particle formation is ignored in comparing the model results to the experimental data.

3.1.1 Benchmark on char temperature and carbon conversion ratio

The intrinsic kinetics model of pulverized coal char burning that includes oxidation and gasification by H_2O has been benchmarked in a previous paper [20], which presents a precise prediction of the temporal evolution of char particle temperature and carbon conversion ratio, particularly at the latter stages of combustion (carbon conversion ratio greater than 80%). By comparing the experimental and modeled char combustion temperature history, the model reveals the ash morphologies in the char particle during char burnout through an integrated model of ash film and ash dilution.

a. Char particle temperature vs. residence time

b. Carbon conversion ratio vs. residence time

Fig. 2 Comparisons of predicted and measured average temperatures and carbon conversion ratio of Pittsburgh bituminous char particle at 1600 K under three different O_2 concentrations, 14 vol% H_2O , 4 vol% CO_2 , and N_2 bath gas. The symbols show the measured data [32] and the lines show the model predictions. The initial char diameter is 115 μm , and initial ash film factor is set to 0.15. (black-and-white in print, and color on Web)

Fig. 2 shows a comparison of the predicted char particle temperature and carbon conversion ratio by the newly developed model that couples a detailed intrinsic char burning model (including oxidization and gasification reactions of H_2O and CO_2 , and considering ash vaporization, ash film, and ash dilution) and a

nano-particle formation model, as described above. Clearly, it can be seen that the predicted values closely follow the experimental measurements, such that the newly developed model can ensure a precise prediction of the char particle combustion temperature and carbon conversion. Meanwhile, it can be seen that the char particle combustion temperature increases with an increase in O_2 concentration. Consequently, the carbon conversion rate increases. The pre-exponential factors for gasification reactions by H_2O and CO_2 (6.0 and 5.0 $kg/s/cm^2/atm^{0.5}$, respectively) have been selected on the basis of the best comparisons of both the char particle combustion temperature and the carbon conversion ratio between model predictions and experiments.

3.1.2 Benchmark on the vaporization of mineral inclusions

Fig. 3 Comparison of predicted and measured fractional vaporization of inclusions of SiO_2 and MgO in both lignite and bituminous coal char particles for a particle size of 55 μm , bath temperature of 1750 K, and 20 vol.% O_2 in O_2/N_2 atmosphere. (black-and-white in print, and color on Web)

The vaporization of mineral inclusions plays a decisive role in the subsequent nucleation, condensation, and resultant nano-particle formation, growth, and distribution. Fig. 3 shows the comparison of predicted and measured vaporized fraction of the major mineral inclusions, SiO_2 and MgO , in North Dakota lignite and Pittsburgh bituminous coal when combusting at 1750 K with 20 vol.% O_2 in a laboratory laminar flow combustor [33]. It can be seen that with the adjustment of the presumed inclusion size the model described here predicts the vaporization of inclusion minerals accurately. Based on past experience, the presumed inclusion sizes needed to accurately predict the vaporization fraction of each metal oxide is consistent across coals of a given rank [29, 34], so the inclusion sizes deduced here should be extendable to similarly ranked coals.

3.1.3 Benchmark on the temporal nano-particle size

Fig. 4 Comparison of predicted and measured volume mean size of nano-particles as a function of residence time during the combustion of Montana lignite at 1750 K with 30 vol.% O₂ in N₂ bath gas for a particle size of 120 μm. (black-and-white in print, and color on Web)

Fig. 4 shows the evolution of nano-particles formed during the combustion of Montana lignite at 1750 K in 30 vol.% O₂ with a particle size of 120 μm. Based on the experimental parameters provided by Neville et al. [4] for pulverized coal (a feeding rate of 5 mg/L, char particles remaining within 0.7 cm of the axis, and MgO accounting for half the mass of the submicron aerosol), a char particle number density of 5.2×10^3 per liter is selected in the modeling. From the agreement between the experiment and kinetic modeling results, it can be seen that there is rapid growth of the nano-particles initially, with slower growth with increasing residence time.

Based on the results shown in Figs. 2–4, the newly developed model describing the char combustion temperature, carbon conversion ratio, vaporization of mineral inclusions, and nano-particle size provides reliable guidance on the kinetic modeling of nano-particle formation and growth. For simplicity, in the work reported here we ignore the interactions of various kinds of vapor molecules originating from different mineral inclusions and take SiO₂ as representative of the sum of all types of mineral inclusions.

3.2 Modeling prediction

3.2.1 Time-resolved formation and growth of nano-particles in O₂/N₂ and O₂/CO₂ atmospheres

a. O₂/N₂

b. O₂/CO₂

Fig. 5 Time-resolved char particle size, temperature, carbon conversion ratio, and the vaporization rate and vaporized fraction of SiO₂ inclusions in O₂/N₂ and O₂/CO₂ atmospheres with 21 vol.% O₂, N₂ or CO₂ bath

gas, bath temperature 1750 K, initial char particle diameter of 55 μm , and SiO_2 inclusion size of 16 μm .

(black-and-white in print, and color on Web)

Fig. 5 shows a comparison of the temporal evolution of char particle size, temperature, carbon conversion ratio, and vaporization rate and vaporized fraction of SiO_2 inclusion in O_2/N_2 and O_2/CO_2 atmospheres. It can be seen that in either O_2/N_2 or O_2/CO_2 the char particle size and temperature decrease with an increase in residence time (or burnout), while the carbon conversion ratio and the vaporized fraction of SiO_2 inclusions increase. However, the vaporization rate of SiO_2 inclusions rapidly decreases as the char conversion becomes large and the char combustion temperature decreases. Also, it can be seen that in comparison with combustion in O_2/N_2 atmospheres, the char particle temperature in O_2/CO_2 atmospheres is significantly lower, primarily because of the endothermicity of char gasification reactions by CO_2 ²¹ [23], but also because of the low diffusivity of O_2 in CO_2 [32, 35]. Despite the lower combustion temperature, the carbon conversion rate is greater in O_2/CO_2 atmospheres due to the contributions of gasification reactions [20, 23]. Hecht et al. [23] pointed out that gasification reactions reduce the rate of char oxidation as a result of the reduced char particle temperature; however, the overall effect of gasification reactions is to increase the carbon conversion rate by approximately 10% in typical oxy-fuel combustion environments. Also, it should be noted that gasification of char carbon by CO_2 produces over twice the volume of CO as does oxidation of the same amount of carbon, as shown by the reaction stoichiometries in R1 and R2.

In comparison with O_2/N_2 atmospheres, both the vaporization rate and vaporized fraction of SiO_2 inclusions in O_2/CO_2 notably decrease. The low char particle temperature in O_2/CO_2 atmospheres causes a low reaction equilibrium constant K_{eq} of R4. In addition, a lower char particle temperature results in a lower $P_{\text{CO}}/P_{\text{CO}_2}$ ratio in the char particle, based on the temperature dependence of the CO/CO_2 production ratio from char oxidation [28]. Consequently, char combustion in O_2/CO_2 atmospheres results in a low partial pressure of SiO at the surface of SiO_2 inclusions and a low vaporization rate and vaporized fraction, and subsequent low extent of vapor saturation and nano-particle nucleation and condensation rate. Overall, the

vaporization rate of SiO₂ inclusions in O₂/CO₂ is more than one order of magnitude lower than that in O₂/N₂.

Figure 6 shows the size distribution of nano-particles formed via nucleation when the char particle is burning, as digitized based on shrinkage of the external diameter of the char particle from 55.0–53.6, 53.6–52.2, 52.2–50.9, 44–42.6, and 38.5–37.1, 33–31.6, and 31.6–30.2 μm, respectively. These nucleated particles subsequently continue growth via condensation until char burnout at a size of 12.4 μm. At the initial char burning stage (i.e, for a char particle diameter of 55.0–53.6 μm), the particle nucleation rate increases with time, because of the increased accumulation of vapor molecules. However, the nucleation rate decreases once significant quantity of nano-particles are formed, as is evident for a char particle size of 53.6–52.2 μm, where a transition is apparent. The nucleated particles provide a large surface area that promotes vapor condensation, and as a result, the decreased concentration of vapor molecules results in decreasing vapor saturation and subsequently a lower particle nucleation rate (as shown for later char particle sizes of 52.2–50.9, 44–42.6, 38.5–37.1, 33–31.6, and 31.6–30.2 μm). With increased char burnout, the SiO₂ vaporization rate continues to slow and even becomes zero at the last stage of burnout (as shown in Fig, 5a). Consequently, the decreased number density of vapor molecules results in a low extent of vapor saturation and nano-particle nucleation rate and a large nucleation particle size (as shown in the last char particle size steps of 38.5–37.1, 33–31.6, and 31.6–30.2 μm).

Fig. 6 Nucleating particle size distribution and size distribution of nano-particles that evolved during different segments of char consumption (denoted by the different stacked plots) for different radial positions within the char particle, as indicated by the key in the top plot. Initial char particle diameter of 55 μm burning in 21 vol.% O₂/N₂ atmosphere at 1750 K. (black-and-white in print, and color on Web)

At the beginning of char combustion (i.e, for a char particle diameter of slightly less than 55.0 μm), fourteen vapor molecules form a cluster or nucleated particle with a size of 1.2 nm. Rapidly thereafter, the nucleated particle size decreases to 0.43 nm and eventually only a single vapor molecule forms a nucleated

particle, because of the increased accumulation of vapor molecules. The critical cluster size increases to 2 vapor molecules when the char particle has shrunk to 44–42.6 μm , to 3–4 when the char particle has shrunk to 38.5–37.1 μm , 12–22 for a size of 33–31.6 μm , and 23–40 for a size of 31.6–30.2 μm . When the char particle has been consumed to less than 30 μm (corresponding to a carbon conversion ratio of 87%), no new nano-sized nucleation particles are formed, because of rapid consumption of vapor molecules through condensation and a low silica vaporization rate. Quann reported that the critical cluster radius for homogeneous nucleation is less than 1.5 nm, and the nano-particles grow to about 2 nm through nucleation and condensation [33]. The model results shown here give similar nano-particle sizes as those reported by Quann.

At the initial char combustion stage, the earlier the formation of nano-particles via nucleation, the larger they grow by condensation until char burnout, and condensation has a significant effect on the nano-particle growth. However, during the last stage of char burnout, such as when the char size is below 38.5 μm (corresponding to a carbon conversion ratio of 72%), the later the formation of nano-particles via nucleation, the larger they are; Nucleation has a dominant effect on particle size, with only a slight increase in particle size due to condensation, because of the decreasing vaporization rate (as shown in Fig. 5a) and the increasing number density of nano-particles, which consume the limited supply of vapor via condensation. Also, for this same reason, the growth rate of particles slows with burnout. Except for decreases in the final particle size and particle number density, char combustion in O_2/CO_2 atmospheres gives similar trends to those found in O_2/N_2 atmospheres.

Once the char has burned out, its temperature rapidly decreases and there is no additional generation of mineral vapor molecules, halting the formation and growth of nano-particles via nucleation and condensation. Even though there are a few residual vapor molecules, their contribution can be ignored because of the large quantity of existing nano-particles. After char burnout, the nano-particles continue to grow via coalescence.

b. O₂/CO₂

Fig. 7 The number and size distribution of nano-particles as a function of char particle residence time in O₂/N₂ and O₂/CO₂ atmospheres. (black-and-white in print, and color on Web)

From Fig. 7, it can be seen that with increased residence time, the nano-particles grow to several tens of nanometer while the particle number density decreases due to coalescence. In the O₂/N₂ atmosphere, the biggest nano-particles grow to approximately 100 nm after a residence time of 2 s (approximately the residence time in power station boilers), and the volume mean size of the nano-particles is about 50 nm. Similar results were reported by Quann et al., wherein the nano-particles grew to 20-100 nm after coalescence [33]. In contrast, in the O₂/CO₂ atmosphere, the biggest nano-particles only grow to about 50 nm, with a corresponding volume mean size of about 30 nm. In comparison with those in the O₂/N₂ atmosphere, the nano-particles shift to smaller size in the O₂/CO₂ atmosphere and the number density is only about 40% as large. This difference is caused by the lower char combustion temperature in the O₂/CO₂ atmosphere, which results in a low vaporization rate and a lower vaporized fraction of mineral inclusions, and subsequently lower formation of nano-particles via nucleation and slower growth via condensation and coalescence. This trend explains why O₂/CO₂ combustion at the same oxygen concentration shifted the submicron particle mode to a smaller size and decreased the yield of submicron particles in experiments reported by Sheng et al [12].

3.2.2 Effect of ambient oxygen content

a. Char temperature and vaporized fraction

b. Nano-particle number density and volume mean diameter

Fig. 8 Effect of oxygen content (12, 21, and 30 vol.%) on the char combustion temperature, vaporized fraction of SiO₂ inclusions, and number density and volume mean diameter of nano-particles in O₂/N₂ and

O₂/CO₂ atmospheres. (black-and-white in print, and color on Web)

Clearly, it can be seen from Fig. 8 that with increased oxygen content, burnout time decreases. In the meantime, an increased char combustion temperature causes a high mineral vaporized fraction, high nano-particle number density, and large particle volume mean diameter. In comparison with that in the O₂/N₂ atmosphere, the lower char burning temperature attributed to the endothermicity of gasification by CO₂ in the O₂/CO₂ environment results in a prolonged burnout time and lower mineral vaporized fraction. A low mineral vaporized fraction means fewer vapor molecules are present, reducing the particle nucleation rate, condensation, and subsequent growth. Consequently, the number density and volume mean diameter of the nano-particles are lower in O₂/CO₂ than in O₂/N₂. Moreover, the differences in particle number density and volume mean diameter in O₂/N₂ relative to O₂/CO₂ increase with increased O₂ content. These differences between N₂ and CO₂ bulk gas primarily develop in the initial half-second and only increase slightly with prolonged residence time.

3.2.3 Effect of particle size

a. Char temperature and mineral vaporization

b. Nano-particle number density and volume mean diameter

Fig. 9 Effect of initial char particle diameter (40, 55, and 70μm) on combustion temperature, mineral vaporization, and number density and volume mean diameter of nano-particles formed in atmospheres consisting of 21 vol-% O₂ in N₂ or CO₂. (black-and-white in print, and color on Web)

Fig. 9 shows comparisons of the char combustion temperature, mineral vaporization fraction and vaporized amount within single char particles, the number density and volume mean diameter of the nano-particles, and the total amount of vaporization under constant fuel feeding rate (or fuel mass) for initial char particles with sizes equal to 40, 55, and 70 μm in both O₂/N₂ and O₂/CO₂ atmospheres. As shown in Fig. 9a, either in O₂/N₂ or O₂/CO₂, the smaller the initial char particle size, the shorter the burnout time and the

higher the particle combustion temperature. High temperature results in high vaporization rate and vaporized fraction. However, the vaporization quantity of inclusions in a large particle is more than that in a small particle because of the greater number of inclusions in larger char particles. Therefore, the larger particle should generate more and larger nano-particles through subsequent nucleation, condensation, and coalescence. On the other hand, as shown in Fig. 9a, the total vaporization amount is higher when small sized char particles are burned at a constant fuel mass feeding rate, because of their greater mineral vaporization fraction. Thus, as shown in Fig. 9b, small char particles generate slightly larger nano-particles at the same number densities as when employing larger char particles. For all of the investigated particle sizes, the nano-particles are fewer and smaller in the O_2/CO_2 atmosphere in comparison with the O_2/N_2 atmosphere.

3.2.4 Effect of ash content

Figure 10 shows the effect of ash content on char combustion and the temporal evolution of the volume mean diameter and number density of nano-particles. With increased ash content, the char particle combustion temperature decreases, and consequently the vaporized fraction of the mineral inclusions in a single char particle decreases, but the mineral vaporization amount from each char particle increases because of its higher ash content. However, the char particles with a low ash content generate a greater total vaporization amount for a constant total ash amount in all char particles per volume, simply because there is a proportionately higher number density of low ash particles. As a result, as shown in Fig. 19b, in both O_2/N_2 and O_2/CO_2 atmospheres the char particles with low ash content generate more and larger nano-particles. On the other hand, the number density and size of the nano-particles formed in an O_2/CO_2 atmosphere are lower than those in an O_2/N_2 atmosphere.

a. Char temperature and mineral vaporization

b. Nano-particle number density and volume mean diameter

Fig. 10 Effect of ash content in char (5, 20, and 35 wt%) on combustion temperature, mineral vaporization,

and number density and volume mean diameter of nano-particles in O_2/N_2 and O_2/CO_2 atmospheres under constant total ash amount in all char particles. (black-and-white in print, and color on Web)

4. Conclusions

A sophisticated intrinsic kinetics model of char particle combustion combining ash film development and char ash dilution with the complex mechanisms of mineral inclusion vaporization within the char particle, homogeneous nano-particle nucleation, heterogeneous condensation, coagulation, and coalescence has been developed. This new model has been used to calculate the temporal evolution of nano-particle number and size during coal char particle combustion at different oxygen contents in O_2/N_2 and O_2/CO_2 atmospheres for char particles with various sizes and ash contents.

The model kinetic rates have been calibrated against (a) char particle temperature and carbon conversion rate measurements for size-classified high-volatile Pittsburgh bituminous coal char particles burning in environments with different oxygen contents, (b) mineral vaporization fraction measurements for major ash components, SiO_2 and MgO , in both North Dakota lignite and Pittsburgh bituminous coal char particles, and (c) measurements of the volume mean size of nano-particles at various residence time during the combustion of Montana lignite. Benchmarking of the model revealed that it can give an accurate prediction of the transient combustion of pulverized coal char particles as well as nano-particle formation and growth, including the temporal evolution of nano-particle number and size.

The model results show that in either O_2/N_2 or O_2/CO_2 atmospheres, the char combustion temperature has a dominant effect on the formation and growth of nano-particles. A high char combustion temperature results in a high partial pressure of vaporized sub-oxides or metals at the surface of inclusions and a high mineral vaporization rate and vaporized fraction, resulting in high vapor saturation and nano-particle nucleation and condensation rates, and consequently more and larger nano-particles. Thus, high oxygen content, low ash content, and small sized char particles, all of which promote high char combustion

temperatures, yield more nano-particles and shift the nano-particle size distribution to larger sizes. In comparison with combustion in O_2/N_2 , both the number density and size of the nano-particles formed in O_2/CO_2 atmospheres are lower, for a given oxygen content in the ambient.

The particle nucleation rate initially increases during char combustion as the mineral vapor concentration increases, and then decreases with char burnout because the nucleated particles provide a large surface area for vapor condensation that rapidly consumes the vapor molecules. Correspondingly, the number of vapor molecules that forms the nano-particle nuclei decreases from several tens of molecules to a single molecule, and then increases to several tens of molecules. Unlike vapor condensation, which contributes to particle growth throughout the lifetime of the char particle, particle nucleation ceases during the last stage of char combustion because of the low mineral vapor concentration and low extent of saturation resulting from a low combustion temperature.

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Figure captions:

Fig.1 Schematic of integrated ash film and ash dilution model (black-and-white in print, and color on Web)

Fig. 2 Comparisons of predicted and measured average temperatures and carbon conversion ratio of Pittsburgh bituminous char particle at 1600 K under three different O₂ concentrations, 14 vol% H₂O, 4 vol% CO₂, and N₂ bath gas. The symbols show the measured data [17] and the lines show the model predictions. The initial char diameter is 115 μm, and initial ash film factor is set to 0.15. (black-and-white in print, and color on Web)

a. Char particle temperature vs. residence time

Fig. 3 Comparison of predicted and measured fractional vaporization of inclusions of SiO₂ and MgO in both lignite and bituminous coal char particles for a particle size of 55 μm, bath temperature of 1750 K, and 20 vol.% O₂ in O₂/N₂ atmosphere. (black-and-white in print, and color on Web)

Fig. 4 Comparison of predicted and measured volume mean size of nano-particles as a function of residence time during the combustion of Montana lignite at 1750 K with 30 vol.% O₂ in N₂ bath gas for a particle size of 120 μm. (black-and-white in print, and color on Web)

Fig. 5 Time-resolved char particle size, temperature, carbon conversion ratio, and the vaporization rate and vaporized fraction of SiO₂ inclusions in O₂/N₂ and O₂/CO₂ atmospheres with 21 vol.% O₂, N₂ or CO₂ bath gas, bath temperature 1750 K, initial char particle diameter of 55 μm, and SiO₂ inclusion size of 16 μm.
(black-and-white in print, and color on Web)

a. O_2/N_2 b. O_2/CO_2

Fig. 6 Nucleating particle size distribution and size distribution of nano-particles that evolved during

different segments of char consumption (denoted by the different stacked plots) for different radial positions within the char particle, as indicated by the key in the top plot. Initial char particle diameter of 55 μm burning in 21 vol.% O_2/N_2 atmosphere at 1750 K. (black-and-white in print, and color on Web)

Fig. 7 The number and size distribution of nano-particles as a function of char particle residence time in O_2/N_2 and O_2/CO_2 atmospheres. (black-and-white in print, and color on Web)

a. O_2/N_2

b. O_2/CO_2

Fig. 8 Effect of oxygen content (12, 21, and 30 vol.%) on the char combustion temperature, vaporized fraction of SiO_2 inclusions, and number density and volume mean diameter of nano-particles in O_2/N_2 and O_2/CO_2 atmospheres. (black-and-white in print, and color on Web)

a. Char temperature and vaporized fraction

b. Nano-particle number density and volume mean diameter

Fig. 9 Effect of initial char particle diameter (40, 55, and 70 μm) on combustion temperature, mineral vaporization, and number density and volume mean diameter of nano-particles formed in atmospheres consisting of 21 vol-% O_2 in N_2 or CO_2 . (black-and-white in print, and color on Web)

a. Char temperature and mineral vaporization

b. Nano-particle number density and volume mean diameter

Fig. 10 Effect of ash content in char (5, 20, and 35 wt%) on combustion temperature, mineral vaporization, and number density and volume mean diameter of nano-particles in O_2/N_2 and O_2/CO_2 atmospheres under constant total ash amount in all char particles. (black-and-white in print, and color on Web)

a. Char temperature and mineral vaporization

b. Nano-particle number density and volume mean diameter

Figure 1

Model hypothesis:

The initial char particle consists of numerous equally spaced concentric shells.
 During the burnout of the outmost shell, some of the ash vaporizes, part of the liberated ash forms ash film, the rest penetrates into the char core, and a new 'outmost' shell is developed.

Figure 2a

Figure 2b

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 6

The special evolution of char size and residence time when initial nano-particles formation via nucleation:

The formation of nano-particles via nucleation and subsequent growth via condensation along with the burnout of char particle or char size changes:

Char diameter: 55.0-53.6 μm
Residence time: 0.0-0.8ms

Char diameter: 53.6-52.2 μm
Residence time: 0.8-1.7ms

Char diameter: 52.2-50.9 μm
Residence time: 1.7-2.7ms

Char diameter: 44.0-42.6 μm
Residence time: 6.5-7.3ms

Char diameter: 38.5-37.1 μm
Residence time: 9.4-10.1ms

Char diameter: 33.0-31.6 μm
Residence time: 12.2-12.9ms

Char diameter: 31.6-30.2 μm
Residence time: 12.9-13.7ms

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9a

Figure 9b

Figure 10a

Figure 10b