Experimental and modeling investigation of oxy-coal combustion: based on Langmuir-Hinshelwood kinetics and direct calculation of char morphology

Liping Chen


State Key Laboratory of Clean Energy Utilization
Zhejiang University, Hangzhou, China
Outline

• Introduction and Background

• Model Derivation
  - Direct calculation of diameter
  - Ash inhibition model
  - Intrinsic LH kinetics

• Model Implement and Results
  - Single particle modeling and CFD modeling
  - DTF and EFR experiments

• Conclusions
Introduction

• Improvements in energy efficiency, availability, fuel flexibility, and capital effectiveness of oxy-fuel coal boilers increasingly rely on CFD modeling

• Accuracy of CFD modeling limited by:
  - Poor knowledge of fundamental coal conversion rate parameter
    • Volatile loss and devolatilisation rate
    • Ignition delay
    • Char combustion rate
  - Limitations of simplified models used to predict coal conversion and heat-flux in CFD simulations
What do we focus on?

Focus on char conversion modeling:

- Direct calculation of particle diameter or apparent density (morphology) in char conversion process

- Ash inhibition effect in char conversion

- Intrinsic Langmuir-Hinshelwood (LH) kinetics applied in oxy-coal combustion
Direct calculation of carbon diameter

**Assumptions**
- Carbon layer in char shrinks
- Ash in char is uniformly distributed and non-active

\[
\rho_{c'} = \frac{m_c}{V_{carbon} + V_{ash}} = \frac{m_c}{V_c} \neq \frac{m_c}{V_{carbon}} \quad (\text{Eq. 1})
\]

\[
V_c = V_{carbon} + V_{ash} = \frac{4\pi r_c^3}{3} \quad (\text{Eq. 2})
\]

(1) Base on the analysis of pure carbon conversion by N.E.L Haugen[2014], the carbon diameter keeps constant before the shrinking of carbon layer:

\[
t \leq \tau
\]

\[
D_c = D_{c0} \quad (\rho_{c'} = \int_0^\tau q_v(r_{periph}, t')dt') \quad (\text{Eq. 3})
\]
Direct calculation of carbon diameter

(2) After the carbon at periphery is completely consumed \((t > \tau)\)

\[
\frac{dr_c}{dt} = - \left( \frac{\partial \rho(r_c,t)}{\partial t} \right) \left( \frac{\partial \rho(r_c,t)}{\partial r} \right)^{-1} = - \frac{1}{v_c} \left\{ \left( \frac{1}{\eta} \frac{dm_c}{dt} \right) \bigg|_o + \left( \frac{1}{\eta} \frac{dm_c}{dt} \right) \bigg|_g \right\} \left( \frac{\partial \rho(r_c,t)}{\partial r} \right)^{-1}; \quad (\text{Eq. 4})
\]

\[
\begin{aligned}
\frac{\partial \rho(r_c,t)}{\partial r} &= F_{\text{oxygen}} + F_{\text{gasification}}; \quad \text{where } F = \frac{kM_c}{v_c} \left( \frac{(1-\phi/\tanh(\phi))}{\text{term1}} \right) \frac{r_c}{\text{term2}} \\
\rho(r_c,t) &= \rho_c^o - \frac{kM_c}{v_c} \left( \frac{I(r_c,t)}{\text{Oxidation}} \right) - \frac{kM_c}{v_c} \left( \frac{I(r_c,t)}{\text{Gasification}} \right) = 0
\end{aligned}
\]

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\frac{\partial \rho(r_c,t)}{\partial r} &= F_{\text{oxygen}} + F_{\text{gasification}}; \quad \text{where } F = \frac{kM_c}{v_c} \left( \frac{(1-\phi/\tanh(\phi))}{\text{term1}} \right) \frac{r_c}{\text{term2}} \\
\rho(r_c,t) &= \rho_c^o - \frac{kM_c}{v_c} \left( \frac{I(r_c,t)}{\text{Oxidation}} \right) - \frac{kM_c}{v_c} \left( \frac{I(r_c,t)}{\text{Gasification}} \right) = 0
\end{aligned}
\]

after complex transformation and simplification, we can obtain:

\[
\frac{dr_c}{dt} = - \frac{3}{4\pi r_c^3 \rho_c^o} \left\{ \left( \frac{1}{\eta} \frac{dm_c}{dt} \right) \left( \frac{1}{1-\phi/\tanh(\phi)} \right) \right\} \quad (\text{Eq. 5})
\]

(only for oxidation or gasification)

\[
\frac{dr_c}{dt} = - \frac{3}{4\pi r_c^3 \rho_c^o} \left\{ \left( \frac{1}{\eta} \frac{dm_c}{dt} \right)_{\text{Oxidation}} \left( \frac{1}{1-\phi/\tanh(\phi)} \right)_{\text{Oxidation}} + \left( \frac{1}{\eta} \frac{dm_c}{dt} \right)_{\text{Gasification}} \left( \frac{1}{1-\phi/\tanh(\phi)} \right)_{\text{Gasification}} \right\} \quad (\text{Eq. 6})
\]

(oxidation and gasification occur simultaneously) (oxy-coal)
Ash around the particle would inhibit the reactant’s diffusion

**Model 1: New Ash Inhibition Model**
( the ash layer won’t collapse)

\[ D_p = D_{p0} \text{ (constant)} \]
\[ \theta_{ashlayer} = 1 - \frac{\rho_{p0} f_{ash0}}{\rho_{ash}} \text{ (constant)} \]
\[ \delta_{ashlayer} = \frac{(D_p - D_c)}{2} \]

**Model 2: New Ash Inhibition Model + Ash layer collapse**
( the ash layer will collapse)

\[ r_p = \frac{3}{\sqrt[3]{3}} (m_{ashout}/\rho_{ash} + 4\pi r_c^3/3)/4\pi \]
\[ \theta_{ashlayer} = 0.17 \]
\[ \delta_{ashlayer} = \frac{(D_p - D_c)}{2} \]

Mass transfer coefficient across the ash film:

\[ K_d = \frac{4\pi r_c D \cdot Sh \cdot r_p \theta_{ashlayer}^{2.5}}{RT_m(\delta_{ashlayer} \cdot Sh \cdot 2 \theta_{ashlayer}^{2.5} r_c)} \]

(CBK model (R.Hurt et al [1998]))
Effect of chemical reaction, reactant penetration, and reaction area could be elucidated in intrinsic LH kinetics

**Reaction rate**

\[
\frac{dm_c}{dt} = \eta m_c S_{carbon} q_{intrinsic}
\]

**Intrinsic reaction rate**

\[
q_{intrinsic} = \frac{(k_1 k_2 p_{O2}^2 + k_1 k_2 p_{O2}) M_c}{k_1 p_{O2} + k_3/2} \quad \text{(oxidation)}
\]

\[
q_{intrinsic} = \frac{k_7 k_4 p_{CO2} M_c}{k_7 + \frac{k_4 p_{CO2} A_7}{A_5} + \frac{k_4' p_{CO} A_7}{A_5} + k_6 p_{H2O} + k_6' p_{H2}} \quad \text{(gasification)}
\]

<table>
<thead>
<tr>
<th>Oxidation mechanism</th>
<th>Gasification mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + O_2 \xrightarrow{kL} C(O)_1 + CO</td>
<td>C + CO_2 \xrightarrow{k_4} C(O)_2 + CO</td>
</tr>
<tr>
<td>C(O)_1 + O_2 \xrightarrow{k_2} C(O)_1 + CO_2</td>
<td>C(O)_2 \xrightarrow{k_5} CO</td>
</tr>
<tr>
<td>C(O)_1 \xrightarrow{k_3} CO</td>
<td>C + H_2O \xrightarrow{k_6'} C(O)_3 + H_2</td>
</tr>
<tr>
<td></td>
<td>C(O)_3 \xrightarrow{k_7} CO</td>
</tr>
<tr>
<td></td>
<td>C + 2H_2 \xrightarrow{k_8} CH_4</td>
</tr>
</tbody>
</table>

The rate constants for each coal will be showed in the following. 

*Slide 8*
The char conversion model is based on the theory of carbon burnout model (CBK) and new developed submodels at current.

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Intrinsic LH kinetics</th>
<th>Diameter Reaction Area</th>
<th>Direct Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Diffusion</td>
<td>Effectiveness Factor $\eta$</td>
<td>Ash Inhibition</td>
<td>New Ash model/(New ash model + ash layer collapses)</td>
</tr>
<tr>
<td>Boundary Diffusion</td>
<td>Single-film Model</td>
<td>Thermal Deactivation</td>
<td>Distributed activation energy model(Hurt et al(1998))</td>
</tr>
<tr>
<td>Particle Temperature</td>
<td>Energy Balance (reaction heat + heat conduction + heat convection + particle radiation)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Single particle conversion modeling

• Reaction Initial Conditions

Atmosphere:  8%O₂-N₂, 8%O₂-CO₂
Temperature:  1173 K, 1473 K, 1600 K
Char particle:  Bituminous coal char; Diameter-100 um;
  Apparent density- 0.45 g/cm³; Ash fraction- 10%;

• Platform:  Matlab

<table>
<thead>
<tr>
<th>Oxidation reactions</th>
<th>Gasification reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{A_1}{A_2} = 3.26 \times 10^{-9} )  ( E = 35 )</td>
<td>( \frac{A_4'}{A_7} = 4.18 \quad E = 51.73 ) (Forward)</td>
</tr>
<tr>
<td>( \frac{A_3}{A_2} = 5.63 \times 10^{-8} )  ( E = 130 )</td>
<td>( \frac{A_7}{A_7} = 1.54 \times 10^{-3} )  ( E = 32.92 ) (backward)</td>
</tr>
<tr>
<td>( A_3 = 3.55 \times 10^{-5} )  ( E = 180 )</td>
<td>( \frac{A_4}{A_5} = 6.92 \times 10^2 )  ( E = 57.72 )</td>
</tr>
<tr>
<td>( A_7 = 3.3 \times 10^4 )  ( E = 38.82 )</td>
<td></td>
</tr>
</tbody>
</table>

The rate constants are calibrated by CBKE and CBKG model respectively
Comparisons between DNS model and current char model

8% O2-N2

**Temperature** 1173 K
- $\rho_e$ DNS
- $\rho_e$ Current Model

**Time (s)**
0 1 2 3 4 5 6

**Temperature** 1473 K
- $\rho_e$ DNS
- $\rho_e$ Current Model

**Time (s)**
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7

**Temperature** 1600 K
- $\rho_e$ DNS
- $\rho_e$ Current Model

**Time (s)**
0 0.1 0.2 0.3 0.4 0.5

DNS Model: Direct Numerical Simulation for single particle (R.E Mitchell et al[2007])

The current model is sufficiently accurate with char conversion modeling.

*Slide 11*
Variations of char morphology and reaction rate in different char morphology models

8% O2-N2

More reasonable descriptions of char properties and reaction rate with direct calculation of diameter.  

Slide 12
Performance of different ash inhibition models

- There is little ash inhibition at low temperature

- A lower reaction rate in new ash inhibition model before ash layer collapse

- In the later burnout stage, collapsed ash layer would increase the burnout time by 7.3% at high temperature.
Effect of gasification on char morphology and burnout time

- Burnout time decreases by 11.1% and 21.3% at 1473 K and 1600 K due to gasification.
- Gasification reaction obviously reduce char density at high temperature.
CFD Modeling: Experiment Conditions

Coal Properties

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_d$  $V_d$  $F_{C_d}$  $Q_d$</td>
<td>$C_{daf}$  $H_{daf}$  $O_{daf}$  $N_{daf}$  $S_{t,daf}$</td>
</tr>
<tr>
<td>Bituminous</td>
<td>6.9  28.7  64.4  29.5</td>
<td>83.4  4.1  11.4  0.9  0.2</td>
</tr>
<tr>
<td>Anthracite</td>
<td>10.7  9.2  80.1  31.8</td>
<td>91.7  3.5  1.3  1.9  1.6</td>
</tr>
</tbody>
</table>

Test Conditions

<table>
<thead>
<tr>
<th>Coal</th>
<th>Reactor</th>
<th>Atmosphere</th>
<th>Coal Flow Rate(kg/s)</th>
<th>Gas Flow Rate(kg/s)</th>
<th>Reactor Temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Primary Gas  Secondary Gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$G_{fl}$  $R_{te}$</td>
<td></td>
</tr>
<tr>
<td>Bituminous</td>
<td>DTF</td>
<td>17.3%O$_2$-CO$_2$</td>
<td>$1.27 \times 10^{-5}$</td>
<td>$1.05 \times 10^{-5}$  $1.93 \times 10^{-4}$</td>
<td>1453</td>
</tr>
<tr>
<td></td>
<td>DTF</td>
<td>26.1%O$_2$-CO$_2$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>$1.05 \times 10^{-5}$  $1.9 \times 10^{-4}$</td>
<td>1453</td>
</tr>
<tr>
<td>Anthracite</td>
<td>EFR</td>
<td>21%O$_2$-79%CO$_2$</td>
<td></td>
<td></td>
<td>1273</td>
</tr>
<tr>
<td>EFR</td>
<td>30%O$_2$-70%CO$_2$</td>
<td>L.Alvarez et al [2013]</td>
<td></td>
<td></td>
<td>1273</td>
</tr>
<tr>
<td>EFR</td>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td>1273</td>
</tr>
</tbody>
</table>

Mesh

EFR: 2D (20,000 mesh)

DTF: 3D (800,000 mesh)

Drop tube furnace system
CFD Modeling: submodels

Setting in CFD

<table>
<thead>
<tr>
<th>Turbulence</th>
<th>RNG model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbulence-chemistry</td>
<td>edc model (simplified global reactions for oxy-fuel combustion (C. Yin et al [2010] )</td>
</tr>
<tr>
<td>Radiation</td>
<td>DO (3 × 3 divisions)</td>
</tr>
<tr>
<td>Particle tracking</td>
<td>DPM</td>
</tr>
<tr>
<td>Devolatilization</td>
<td>single-rate kinetic model</td>
</tr>
<tr>
<td>Char combustion</td>
<td>UDF</td>
</tr>
</tbody>
</table>

Kinetic constants for anthracite in char conversion

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<td>$E = 35$</td>
</tr>
<tr>
<td>$A_2 = 5.63 \times 10^{-8}$</td>
<td>$E = 130$</td>
</tr>
<tr>
<td>$A_3 = 4.72 \times 10^6$</td>
<td>$E = 180$</td>
</tr>
<tr>
<td>$A_4 = 2.28$</td>
<td>$E = 58.72$ (Forward)</td>
</tr>
<tr>
<td>$A_7 = 1.54 \times 10^{-3}$</td>
<td>$E = 32.92$ (Backward)</td>
</tr>
<tr>
<td>$A_5 = 6.92 \times 10^2$</td>
<td>$E = 57.72$</td>
</tr>
<tr>
<td>$A_7 = 6.3 \times 10^6$</td>
<td>$E = 45.82$</td>
</tr>
</tbody>
</table>
Temperature profile

EFR temperature profile (scaled to 0.4 m)  DTF temperature profile

Slide 17
• Burnout fraction increase by 0.7% due to gasification.

• Different ash inhibition models have similar performance due to low temperature.
Conclusions

- Correlations for direct calculation of char diameter in oxy-coal combustion were established, as well as an ash inhibition model and a char conversion model based on intrinsic LH kinetics.
- Direct calculation of char diameter provides an reasonable reaction rate and char morphology both at high or low temperature, while power law result in a lower reaction rate and char burnout.
- Gasification reaction has a great influence not only on char burnout time directly (decreased by 21.3% at high temperature), but also on char morphology.
- Char conversion model have excellent performance in single particle conversion and furnace modeling, where its burnout fraction is agree well with experimental value (maximal deviation less than 3%)
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Thanks for your attention !!!

E-mail: lipingchen@zju.edu.cn