Characterization of Coal and Biomass Conversion Behaviors in Advanced Energy Systems

Reginald Mitchell, Paul Campbell and Liqiang Ma

High Temperature Gasdynamics Laboratory
Thermosciences Group
Mechanical Engineering Department
Stanford University, Stanford, CA

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Motivation and Project Objectives

Motivation

The coal-fired power plant will be the workhorse for electric power generation for more than the next 50 years, especially in the United States and China. With the advances made in refractory materials, burner designs, high-temperature heat exchangers, and integrated gasification combined cycle and hybrid technologies, coal-fired power plants have the potential to be energy efficient, environmentally benign suppliers of chemicals, transportation fuels, and hydrogen as well as electricity.

Objectives

Fundamental studies on coal and biomass combustion and gasification phenomena are undertaken in order to gain the understanding needed to develop models that predict accurately coal and biomass conversion behaviors in environments likely to be established in advanced energy systems.
Advanced Gasification-Based Systems

The models being developed will provide the capability to predict coal and biomass conversion behaviors in advanced energy systems such as that envisioned below.

Hybrid Technology

The models being developed will provide the capability to predict coal and biomass conversion behaviors in advanced energy systems such as that envisioned below.

Coal gasifier integrated with an advanced coal combustor. Limestone is added to the gasifier and combustor for $\text{SO}_x$ capture. [A system concept from the DOE - Fossil Energy website http://www.fossil.energy.gov/programs/powersystems/combustion/]
Outline of Presentation

• Introduction, Motivation and Objectives
• Reactivity and Mode of Particle Burning Studies
• Elevated Pressure Studies
• Oxygen-Enhanced Combustion Studies
• High-Pressure Facility
• Conclusions
Char Reactivity and Mode of Burning Studies
Coal Combustion Processes

- Devolatilization
- Oxidation
- Fragmentation

Zone I → Zone II → Zone III
Motivation and Objectives

Motivation

Under pulverized coal combustion conditions, char particles burn with reductions in both diameter and apparent density. The specific surface areas of chars also vary during mass loss.

The manner in which diameter, apparent density, and specific surface area vary with mass loss during char conversion at moderate to high temperatures cannot be described accurately with present-day models.

Objectives

The overall objective is to develop the capability to predict accurately the chemical and physical characteristics of char particles undergoing mass loss at both low and high temperatures. Efforts are directed towards developing and validating models for char reactivity, mode of burning, and specific surface area evolution that depend upon the instantaneous state of the char.
Examples of Materials Tested

<table>
<thead>
<tr>
<th>Almond Shells</th>
<th>Wood Chips</th>
<th>Non-Recyclable Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Straw</td>
<td>Tree Prunings</td>
<td>Lower Kittanning Coal</td>
</tr>
</tbody>
</table>
Synthetic Chars

The use of synthetic chars allows the study of char combustion and gasification without the complications of unknown chemical composition and unknown porosity inherent in real coals and without the possible catalytic effects of ash.

θ = 16%

θ = 25%

θ = 36%
Laminar Flow Reactor

**Pressure:** 1 atm
**Temperature:** 1250 – 2100 K
**[O₂]:** 0 – 21%
Pressurized TGA

Composition: inert and oxidizing
Pressure = \(10^{-5}\) torr – 100 atm
Temperature = up to 1373 K
Weight Range = 0 – 10g
Accuracy = \(10^{-6}\)g
SEMs of Partially Oxidized Chars

Synthetic char
θ = 25%

$t = 0$
$m/m_0 = 1.0$
$\rho_a = 1.21 \text{ g/cm}^3$
$D = 67.5 \mu m$
$s_g = 177 \text{ m}^2/\text{g}$

$t = 47 \text{ ms}$
$m/m_0 = 0.77$
$\rho_a = 1.18 \text{ g/cm}^3$
$D = 56.6 \mu m$
$s_g = 243 \text{ m}^2/\text{g}$

$t = 72 \text{ ms}$
$m/m_0 = 0.61$
$\rho_a = 1.15 \text{ g/cm}^3$
$D = 49.8 \mu m$
$s_g = 246 \text{ m}^2/\text{g}$

$t = 95 \text{ ms}$
$m/m_0 = 0.50$
$\rho_a = 1.11 \text{ g/cm}^3$
$D = 41.6 \mu m$
$s_g = 248 \text{ m}^2/\text{g}$

$t = 117 \text{ ms}$
$m/m_0 = 0.46$
$\rho_a = 1.12 \text{ g/cm}^3$
$D = 41.6 \mu m$
$s_g = 246 \text{ m}^2/\text{g}$
Intrinsic Char Reactivity

Heterogeneous Reaction Mechanism

\[
\begin{align*}
2 \cdot -C + O_2 & \xrightarrow{k_1} -C(O) + CO \\
-C + -C(O) + O_2 & \xrightarrow{k_2} -C(O) + -C + CO_2 \\
-C + -C(O) + O_2 & \xrightarrow{k_3} -C(O) + -C(O) + CO \\
-C(O) & \xrightarrow{k_4} -C + CO
\end{align*}
\]

Intrinsic char reactivity:

\[
R_{iC} = \hat{M}_C \left( RR_1 + RR_2 + RR_3 + RR_4 \right)
\]

Adsorbed oxygen atom site fraction:

\[
\frac{d\theta_O}{dt} = \left( \frac{N_{AV}}{S} \right) \left( RR_1 + RR_3 - RR_4 \right)
\]
Almost all char combustion models that attempt to account for variations in particle size and apparent density during burning employ the empirically based power-law equations.

**Power-law relations**

\[
\frac{\rho}{\rho_0} = \left(\frac{m}{m_0}\right)^\alpha \quad \frac{D}{D_0} = \left(\frac{m}{m_0}\right)^\beta,
\]

For spherical particle: \( \alpha + 3\beta = 1 \)

**Zone I:** particles burn at constant diameter, \( \alpha = 1, \beta = 0 \)

**Zone III:** particles burn at constant density, \( \alpha = 0, \beta = 1/3 \)

**Zone II:** particles burn with decreases in both size and apparent density, \( 0 < \alpha < 1 \) and \( 0 < \beta < 1/3 \)

**A short-coming of this model**

The parameters \( \alpha \) and \( \beta \) are constants, thus the manner in which apparent density and diameter vary with mass loss during the early stages of burning is the same as that during the late stages.
An isothermal, spherical char particle, initially of size $D_{p0}$, apparent density $\rho_{C0}$ and specific surface area $S_{gC0}$, is divided into $K$ concentric annular volume elements, $V_k$. The mass in each element is oxidized at a rate dependent on local conditions.

**Local rate of mass loss**

$$\frac{1}{m_{C,k}} \frac{dm_{C,k}}{dt} = R_{iC,k}S_{gC,k}$$

**Internal Oxygen Diffusion**

$$\frac{\partial C_{O2}}{\partial t} - \frac{1}{r^2} \frac{d}{dr} \left( r^2 D_{eff} \frac{\partial C_{O2}}{\partial r} \right) = -\hat{R}_{iO2} \rho_C S_{gC} = -R_{iC}V_{O2} \rho_C S_{gC} / \hat{M}_C$$

**Local conversion, apparent density and surface area**

$$x_{C,k} = 1 - m_{C,k}/m_{C0,k} \quad \rho_{C,k} = m_{C,k}/V_k \quad S_{gC,k} = S_{gC0,k} \left( 1 - x_{C,k} \right) \left( \frac{\rho_{C0,k}}{\rho_{C,k}} \right) \sqrt{1 - \psi \ln(1 - x_{C,k})}$$

**Overall conversion, apparent density and specific surface area**

$$m_C = \sum_k m_{C,k} \quad \rho_C = m_C / \sum_k V_k \quad S_{gC} = \sum_k \left( S_{gC,k} m_{C,k} \right) / m_C$$
Char Conversion Model

**Overall Particle Burning Rate (per unit external surface area)**

These expressions relate the oxygen partial pressure at the external surface of the particle to that in the ambient gas.

\[ q = \frac{k_d P}{\gamma} \ln \left( \frac{1 - \gamma P_s / P}{1 - \gamma P_g / P} \right) = \left( 1 + \frac{\eta D_p \rho_C S_{gC}}{6} \right) R_{iC, ex} \]

**Particle Effectiveness Factor**

\[ \eta = \frac{\sum_k \hat{R}_{iO_2,k} \rho_{C,k} S_{gC,k} V_k}{\sum_k \hat{R}_{iO_2,max} \rho_{C,k} S_{gC,k} V_k} = \frac{\sum_k \hat{R}_{iO_2,k} \rho_{C,k} S_{gC,k} V_k}{\sum_k \hat{R}_{iO_2,ex} \rho_{C,k} S_{gC,k} V_k} \]

**Char Particle Temperature**

\[ q \Delta H = - \frac{Nu \lambda}{D_p} \kappa \frac{\kappa}{1 - e^{\kappa}} (T_p - T_g) + \varepsilon \sigma (T_p^4 - T_w^4) \]

\[ \kappa = \frac{\gamma c_{p,g} D_p \nu O_2 q}{\hat{M}_C \lambda Nu} \]
In the low temperature, Zone I burning regime, the particle is totally penetrated by oxygen. The oxygen concentration inside the particle is uniform.

The power-law mode of burning model with constant parameters accurately describes changes in this constant diameter burning regime.

\[ \frac{\rho_c}{\rho_{c0}} = \left( \frac{m_c}{m_{c0}} \right) \]
\[ \frac{D}{D_0} = \left( \frac{m}{m_0} \right)^\vartheta = 1 \]

Specific surface area follows the Bhatia-Perlmutter random pore model.

\[ S_{gC} = S_{gC0} \left( 1 - x_c \right) \left( \frac{\rho_{c0}}{\rho_c} \right) \sqrt{1 - \psi} \ln \left( 1 - x_c \right) \]
In the Zone II burning regime, an oxygen concentration gradient exists inside the char particle. Under weak zone II burning conditions (which occur at moderate temperatures), burning initially occurs at constant diameter before a transition to variable size and density burning at high extents of conversion.

The power-law mode of burning model with constant parameters can not describe accurately the changes in this burning regime.

$$\frac{\rho_c}{\rho_{c0}} = \left(\frac{m_c}{m_{c0}}\right)^\alpha$$

$$\frac{D}{D_0} = \left(\frac{m}{m_0}\right)^\beta$$

Initially, $\alpha = 1$, $\beta = 0$. In the late stages of burning, $\alpha = 0.4$, $\beta = 0.2$

No model has been developed that describes the evolution in specific surface area.
Burning Behavior: Strong Zone II Burning

At high temperatures (strong zone II burning conditions), burning occurs with reductions in size and apparent density after a very short initial period of nearly constant diameter burning.

The power-law mode of burning model with constant parameters somewhat describes the changes in this burning regime.

\[
\frac{\rho_c}{\rho_{c0}} = \left(\frac{m_c}{m_{c0}}\right)^\alpha
\]

\[
\frac{D}{D_0} = \left(\frac{m}{m_0}\right)^\beta
\]

Initially, \( \alpha = 1, \beta = 0 \). During the middle to late stages of burning, \( \alpha = 0.1, \beta = 0.3 \).

No model has been developed that describes the evolution in specific surface area.
The effectiveness factor can be expressed in terms of the Thiele modulus and a parameter $m$ that can be determined from fits to the calculated $\eta–\phi$ relation.

The $\eta–\phi$ relation can be approximated by the expression

$$\eta = \frac{3}{\phi_m} \left( \frac{1}{\tanh(\phi_m)} - \frac{1}{\phi_m} \right)$$

where

$$\phi_m = \phi \sqrt{(m + 1)/2}$$

and where the Thiele modulus is defined as

$$\phi = \left( \frac{D_p}{2} \right) \sqrt{\frac{\hat{R}_{iO_2,ex} \rho_C S_{gC}}{C_{O_2,ex} D_{eff}}}$$
Summary: Burning Mode

At both low and high temperatures, oxygen nearly completely penetrates the particle before the onset of significant oxidation.

Under zone I burning conditions (T < 900 K), the power-law mode of burning model is adequate, assuming constant diameter burning. Specific surface area evolves in accord with random pore models.

Under zone II burning conditions, power-law mode of burning relations with constant parameters cannot describe accurately the reductions in particle diameter and apparent density over the entire lifetime of a burning particle.

No model has been put forth that accurately characterizes the variations in specific surface area while burning under zone II conditions.

For the reaction mechanism employed, the effectiveness factor can be related to the Thiele modulus using the following expression:

\[
\eta = \frac{3}{\phi_m} \left( \frac{1}{\tanh(\phi_m)} - \frac{1}{\phi_m} \right)
\]

where \( \phi_m = \phi \sqrt{(m + 1)/2} \)
Char Reactivity to Oxygen at Elevated Pressures
Motivation and Objectives

Motivation

Pressurized gasification and combustion of fossil fuels have the advantages of increased conversion efficiency, decreased pollutant emissions, and reduced furnace size.

Despite the numerous studies concerned with char oxidation, the database on pressurized char reactivity to oxygen is rather limited. The data are insufficient to answer some of the most rudimentary questions concerning the impact of pressure on char reactivity.

Objectives

Increase the data available on the conversion rates of coal chars at elevated pressures.

Use the data to characterize the separate effects of total pressure and oxygen mole fraction on char reactivity.
Effects of Total Pressure

Char reactivities @ total pressures $P = \{1, 4, 8\}$ atm
constant $y_{O_2} = 6\%$

At $x_C = 0.4$, when $P$ increase from 1 → 8 atm,
$T = 773$ K, $R_{iC}$ increase from $\sim 0.13 \times 10^{-6} \rightarrow \sim 0.53 \times 10^{-6} \text{ g·m}^{-2}·\text{s}^{-1}$,
$T = 823$ K, $R_{iC}$ increase from $\sim 0.71 \times 10^{-6} \rightarrow \sim 1.48 \times 10^{-6} \text{ g·m}^{-2}·\text{s}^{-1}$.

Intrinsic reactivity $R_{iC}$ increases with increasing total pressure at constant oxygen mole fraction.
Effects of Oxygen Mole Fraction

Char reactivities @ oxygen mole fraction $y_{O2} = \{3\%, 6\%, 12\%\}$
constant $P = 8$ atm

At $x_c = 0.4$, when $y_{O2}$ increase from 3\% → 12\%,
$T = 773$ K, $R_{iC}$ increase from $\sim 0.23 \times 10^{-6}$ → $\sim 0.84 \times 10^{-6}$ g·m⁻²·s⁻¹,
$T = 723$ K, $R_{iC}$ increase from $\sim 0.06 \times 10^{-6}$ → $\sim 0.25 \times 10^{-6}$ g·m⁻²·s⁻¹.

Intrinsic reactivity $R_{iC}$ increases with increasing oxygen mole fraction at constant total pressure.
Effects of Oxygen Partial Pressure

Char reactivities @ constant oxygen partial $P_{O_2} = 0.24$ atm

- For the same $T$ and $P_{O_2}$, the reactivity $R_{iC}$ is almost the same during the entire range of conversion regardless of total pressure $P = \{2, 4, 8\}$ atm.
- Reactivity increases with increasing oxygen partial pressure $P_{O_2}$
At given $T$, the reactivity is solely determined by oxygen partial pressure ($P_{O_2} = y_{O_2} P$), independent of the individual values of total pressure $P$ and oxygen mole fraction $y_{O_2}$. 
**Comparisons: Experiment vs Calculation**

**R_{iC} profile vs. conversion:**
1. Initial rapid increase with conversion up to about 10% to 20% conversion.
2. Slower increase or even steady.
3. Increase in the late stages of burning.

Data points: experiments
Dashed curves: calculations employing the reaction mechanism

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>A*</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) $2, C_f + O_2 \rightarrow CO + C(O)$</td>
<td>$2.61 \times 10^2$</td>
<td>44.6</td>
</tr>
<tr>
<td>(R2) $C_f + C(O) + O_2 \rightarrow CO_2 + C(O) + C_f$</td>
<td>$5.15 \times 10^{11}$</td>
<td>166.2</td>
</tr>
<tr>
<td>(R3) $C_f + C(O) + O_2 \rightarrow CO + C(O) + C(O)$</td>
<td>$1.88 \times 10^{17}$</td>
<td>275.9</td>
</tr>
<tr>
<td>(R4) $C(O) \rightarrow CO + C_f$</td>
<td>$1.09 \times 10^{12}$</td>
<td>267.1</td>
</tr>
</tbody>
</table>

* units consistent with surface concentrations in mol/m²-surface, gas concentrations in mol/m³-fluid, and time in s.
Total pressure has no effect on char reactivity at constant oxygen partial pressure. In the zone I burning regime, at fixed $T$, char reactivity is determined solely by the oxygen partial pressure $P_{O_2}$, independent of the individual values of total pressure $P$ and oxygen mole fraction $y_{O_2}$. [Recall that $P_{O_2} = P y_{O_2}$].

Intrinsic char reactivity increases with increasing total pressure for a fixed oxygen mole fraction.

For a given total pressure, the intrinsic reactivity increases with oxygen mole fraction.

The 4-step reaction mechanism can describe char oxidation under zone I burning conditions at atmospheric as well as elevated pressures.

The transition temperature from zone I to zone II burning decreases with increasing total pressure, and char oxidation at elevated pressures favors the burning regime of zone II controlled by pore diffusion.
Oxygen-Enhanced Combustion
Motivation and Objectives

Motivation

Increasing the oxygen content of the oxidizer enhances product throughput, increases system efficiency, yields a flue gas having a relatively high CO$_2$ concentration, and reduces the carbon in ash. Combined with the latest advances in low-temperature oxy-fuel burner designs, nitrogen oxide emissions (NO$_x$) can also be reduced with oxygen-enriched combustion.

The database on coal and biomass reactivity to oxygen at high O$_2$ partial pressures is sparse. Kinetic parameters that describe char reactivity to oxygen have not been tested at high oxygen concentrations.

Objectives

Increase the data available on the conversion rates of coal and biomass chars at O$_2$ concentrations greater than 21%, by volume.

Use the data to characterize the effect of oxygen mole fraction on char reactivity.
Oxygen-Enhanced Combustion

Pulverized biomass particles burning in the laminar flow reactor. Gas temperatures are nominally 1350 K.

- trace O$_2$, ppm range
- 3% O$_2$, by volume
- 24% O$_2$, by volume
- 48% O$_2$, by volume
High-Pressure Gasification and Combustion Facility
Motivation and Objectives

Motivation

Elevated pressures are used in advanced energy conversion systems that employ integrated gasification combined cycle (IGCC) technology. Fundamental understanding of the effects of pressure on coal and biomass conversion rates and morphology is essential to the development of these technologies.

Devolatilization and char conversion models have not been developed to the extent that mass loss phenomena can be predicted accurately in pressurized gasifiers and combustors.

Objectives

Characterize the effects of pressure on coal and biomass conversion phenomena and develop and validate models that predict accurately the impact of pressure on char-particle morphology and char reactivity.

Assess the impact of fragmentation on conversion rates at high pressures.
High-Pressure Reaction Facility

The high-pressure facility will permit coal and biomass devolatilization and char conversion studies at the temperatures and heating rates typical of advanced pressurized gasifiers and combustors.
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