Drying, devolatilization & char oxidation of solid fuel

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Doctor of Technology

Åbo Akademi 2016:
Chemistry in Combustion Processes
Where does the electricity come from globally?

(IEA 2014)
Solid fuel combustion
In pulverized fuel combustion, size of fuel pieces also called particles are around 0.1 mm.
Solid fuel combustion

What happens with the mass of one 0.1 mm single fuel particle in this furnace?

- Drying
- Devolatilization
- Char oxidation

Graph:
- Mass
- Time (0.2 s, 0.4 s, 0.6 s)

Diagram:
- Fuel input
- Process stages (drying, devolatilization, char oxidation)
- Mass change over time
Terms and concepts

• Small vs large fuel particle
• Devolatilization/pyrolysis of small and large particles
• Char oxidation of small and large particles
• Kinetic regime
• Mass transfer regime
• Chemical kinetics control
• Mass transfer control
• Char gasification
• Gasification
• Coal types
• Difference in burning between coal and biomass
• Oxy-combustion
H₂O → Drying
Volatile matter → Devolatilization
Char → Oxidation
Ash → Ash
• less volatile matter, and less moisture in coal than in biomass
• coal forms more char than biomass
Drying

Fuel + heat → water vapor

(endothelial: $\Delta H > 0$)
Energy balance during drying of a small (<0.1 mm) fuel particle

\[
m_p c_p \frac{dT_p}{dt} = h S_p \left( T_{\text{gas}} - T_p \right) + \frac{dm_p}{dt} \Delta H + S_p \varepsilon_p \sigma \left( T_R^4 - T_p^4 \right)
\]

- Convective heat transfer
- Energy consumption
- Radiation heat transfer

\[
h = \frac{k_{\text{gas}} Nu}{d}
\]

- Specific heat
- Mass
- Temperature
- Vaporization enthalpy
- External surface area
- Surface emissivity
Devolatilization - pyrolysis

Fuel + heat $\rightarrow$ volatiles + char  \[ (\Delta H \approx 0) \]

Volatile composition:
- CO
- CO$_2$
- H$_2$
- H$_2$O
- Hydrocarbons
- Tars

Exact volatile composition depends on the heating rate
Devolatilization - pyrolysis

As the volatiles are oxidized, a flame can be observed.
Devolatilization of wood

• Hemicellulose start pyrolyzing at 200-350 °C
• Cellulose start pyrolyzing at 280-375 °C
• Lignin start pyrolyzing at 250-500 °C
• Certain extractives such as terpenes (few % in wood) start pyrolyzing at less than 225 °C
Hemicellulose

Cellulose

Lignin

Di Blasi 2008
Devolatilization of coal

- Fossil coals can be divided into anthracite, bituminous coal and lignite
- Volatile matter very low for anthracites
- Volatile content higher for lignite than for bituminous coals
Devolatilization of lignite

- **Lignite**: starts to pyrolyse at 300-400 °C releasing CO and CO$_2$
- At around 400-700 °C also hydrocarbon vapors, tars and H$_2$ are produced
Devolatilization of bituminous coals

- **Bituminous coals** becomes plastic and can swell remarkably during pyrolysis.
- CO and CO$_2$ is formed but to a less extent than for lignite, due to lower oxygen content.
- Tars, hydrocarbons, and soot are formed at temperatures higher than 400 °C.
Devolatilization of anthracite

- Low volatile content of anthracite
What happens with $T$ for a 0.05 mm wood particle if we put in 1000 °C?

What happens with $T$ for a 6 mm wood particle if we put in 1000 °C?
Drying and devolatilization: in sequences or simultaneously?

• For small particles (< 0.1 mm), drying and devolatilization occurs in sequences

• For large particles, drying and devolatilization occurs partly simultaneously due to temperature gradients inside the particle
Drying and devolatilization: in sequences or simultaneously?

How do we determine this?

\[ Bi = \frac{r h_{\text{eff}}}{k_{c, \text{particle}}} \]

High Bi → temperature gradient significant

Low Bi → temperature gradient negligible
Char

- Char yield of wood around 15% on dry basis
- Char yield of coal up to more than 90% on dry basis

Devolatilization  Char Oxidation
Biomass char yield slightly dependent on heating rate

(Di Blasi 2011)
Coal char yield strongly dependent on heating rate.

(Kobayashi et al. 1976)
Char

Biomass
Lignite
Bituminous coal
Anthracite

HHV (MJ/kg)_{db}

Char yield % (dry basis)

Aging
Char Oxidation generally significantly slower than Devolatilization: important to consider in the design of combustion units.
Char

• Organic and inorganic part
• Organic part consists of C, N, O, S, H
• Of the organic part, almost 100% on mass basis is C
• Oxidation of char refers to heterogeneous oxidation of solid carbon, C(s)
• Heterogeneous combustion:
  \[ C(s) + O_2(g) \rightarrow CO_2(g) \]
• Homogeneous combustion:
  \[ 2CO(g) + O_2(g) \rightarrow 2CO_2(g) \]
Char oxidation

\[ \text{C(s)} + \text{O}_2 (g) \rightarrow \text{CO/CO}_2(g) \quad (\Delta H < 0) \]

\[
m_p c_p \frac{dT_p}{dt} = h S_p \left( T_{gas} - T_p \right) + \frac{dm_p}{dt} \Delta H + S_p \varepsilon_p \sigma \left( T_R^4 - T_p^4 \right) \]

\[ T_p > T_{gas} \]

\[ < 0 \]
Char oxidation

- Char is porous
- Oxidation reactions occur inside char particle and at the external surface of the char particle
The faster the reaction (kinetics), the shorter way the oxygen will penetrate inside the char.

If the reactions are very fast, all the reactions take place at the external surface.
$O_2$ concentration inside and outside char particle
Char oxidation

- limited by *mass transfer* if particles are large (>1 mm)
- limited by *chemical kinetics* if particles are small (<0.05 mm)
- Otherwise limited by the combined effects of *chemical kinetics* and *mass transfer*
(For a typical bituminous coal char, note that the diagram is fuel dependent)
Chemical kinetics control (Regime I)

- Fuel type and mass limits the char oxidation rate
- Char oxidation rate is strongly temperature dependent
- Rate not limited by external mass transfer

Mass transfer control (Regime III)

- External surface limits char oxidation rate
- Char oxidation rate is not strongly temperature dependent
Chemical kinetics control (Regime I & Regime II)

- High internal surface area gives high kinetic rate
- Biomass chars have higher internal surface area (up to 1000 m$^2$/g) than coal chars (10-100 m$^2$/g)
- Catalytic elements such as Na, K, Mg, Ca can reduce activation energy and enhance rate
- Biomass char has higher fraction of catalytically important elements than coal char

Biomass chars significantly more reactive than coal chars with respect to O$_2$
\[
\frac{dm}{dt} = A_i m \eta c_{O_2} A e^{-E/RT_P}
\]

RIII => \( \eta \rightarrow 0 \)

RI => \( \eta = 1 \)

- Low \( E \) gives high rate
- High \( T_p \) gives high rate

- For coal chars \( E \) is around 160 kJ/mol for char oxidation by \( O_2 \)
- For biomass chars \( E \) is generally around 100 kJ/mol for char oxidation by \( O_2 \)
Char oxidation and char gasification

- In combustion, char is always oxidized to some extent by CO$_2$ and H$_2$O
- Char oxidation by CO$_2$ and H$_2$O is called *char gasification*
- *Char gasification* reactions are important in combustion systems and gasification systems
- Note: char gasification and gasification have different meaning
Char oxidation

Char particle \rightarrow \text{CO} \quad \text{exothermic}

Char gasification

Char particle \rightarrow 2\text{CO} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}_2 \quad \text{endothermic}
Combustion

Fuel → Air → Electricity → Heat

N₂, CO₂

Gasification

Fuel → Insufficient amount of air

Some CO₂ → CO, H₂
Gasification

• In combustion the carbon and hydrogen reacts to $\text{CO}_2$ and $\text{H}_2\text{O}$

• In gasification, the goal is to produce a gas rich in CO and $\text{H}_2$ that for example can be burned in a gas boiler

• In gasification systems an insufficient amount of air is used, so that the oxidation of gases is incomplete → high levels of CO and $\text{H}_2$
Waste gasification in Lahti

1. Fuel handling
2. FB gasifier
3. Gas cooling
4. Gas filter
5. Gas fired boiler
Oxy-combustion

• A combustion technique for the future?
• Fuels are combusted in O\textsubscript{2} instead of air
• To avoid extremely high temperatures, the CO\textsubscript{2} is partly recirculated
• The goal is to produce electricity, but so that the formed CO\textsubscript{2} is stored
Combustion

- Coal
- Air
- O₂
- N₂, CO₂
- heat
- electricity

Oxy-combustion

- Coal
- O₂
- CO₂
- heat
- electricity
- Storage
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...stay tuned for part II of this course

THANK YOU for your ATTENTION!