The Clean Energy Transition Partnership

Mathematical modeling for deeper insight into single droplet experiments relevant for black liquor oxy-combustion

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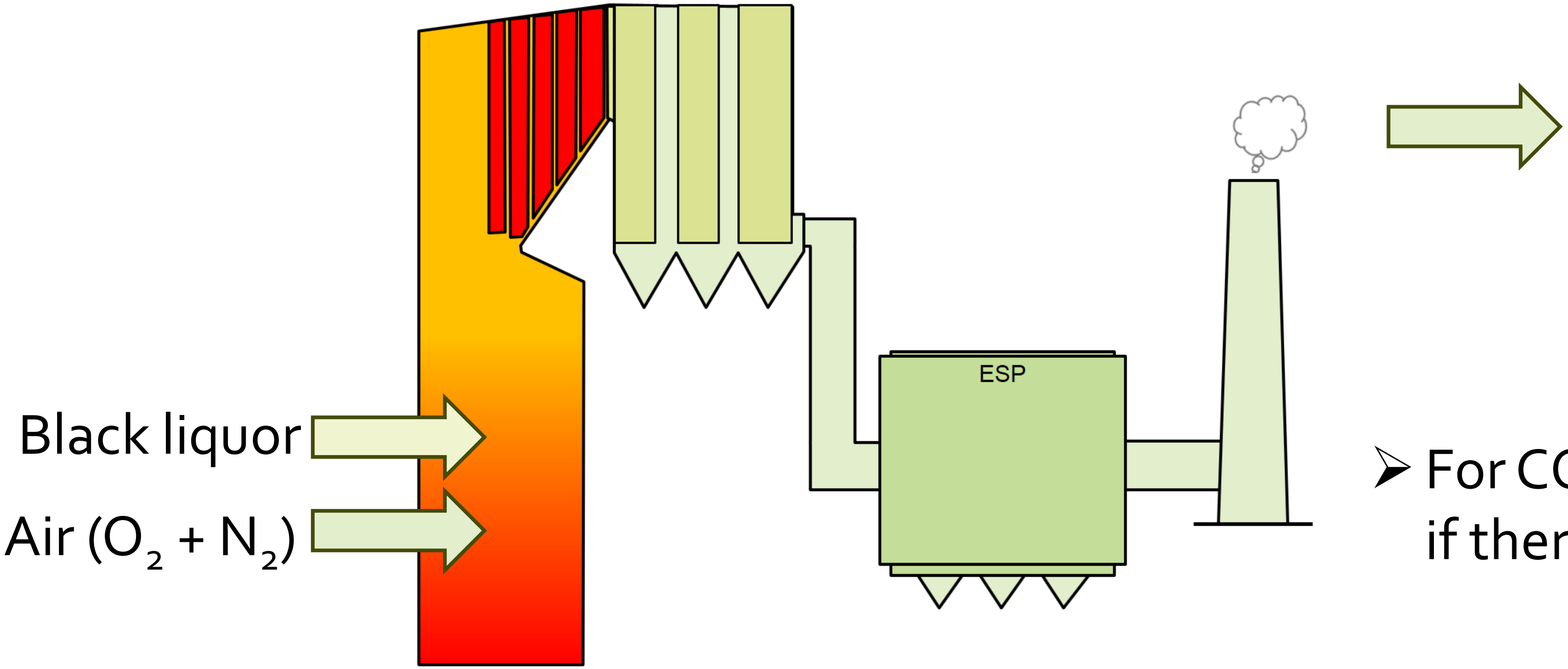
Oxy-Kraft

Oxy-fired black liquor recovery boiler

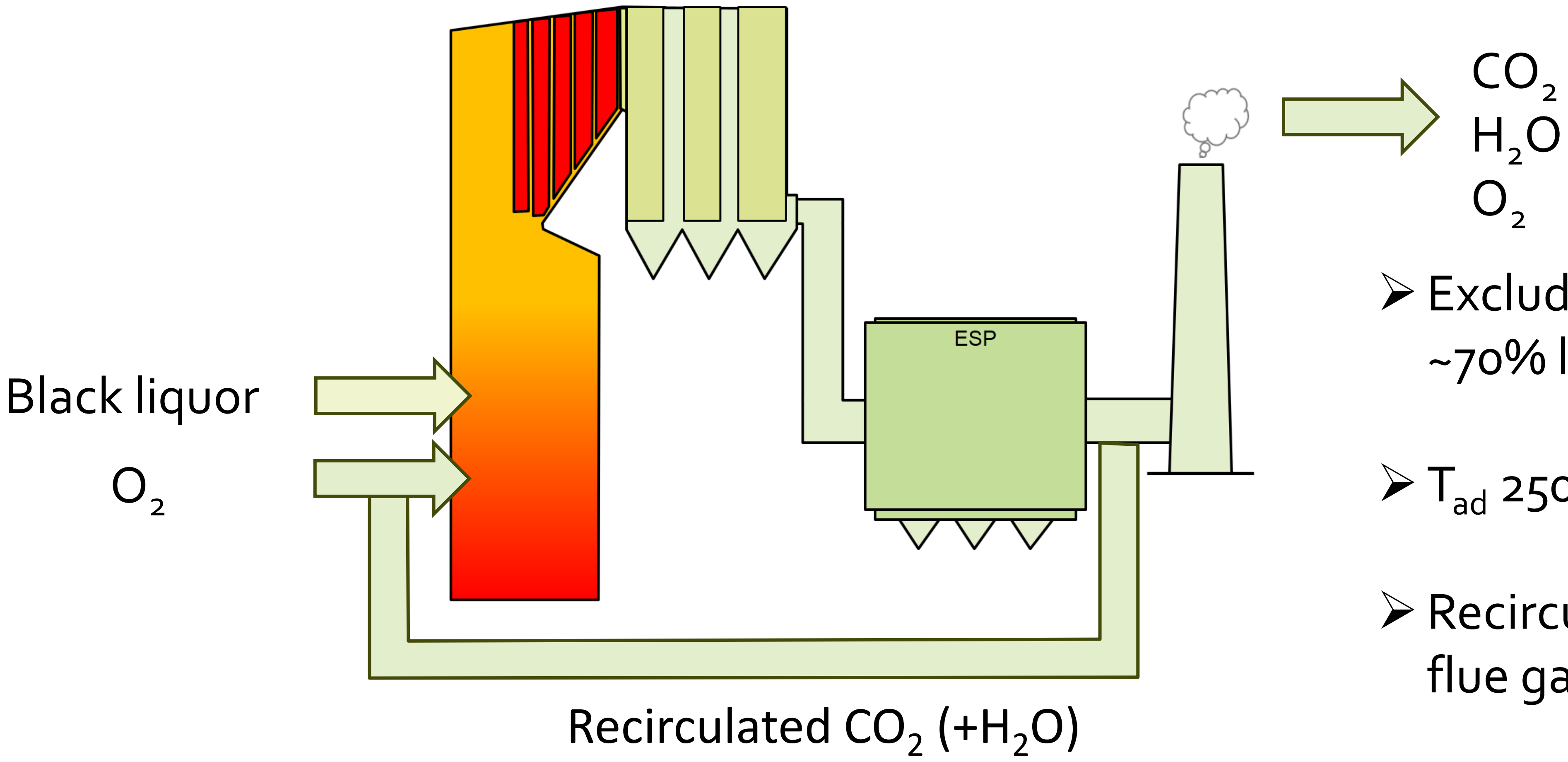
Traditional air-combustion



13 vol-% CO_2
17 vol-% H_2O
3 vol-% O_2
67 vol-% N_2

- For CO_2-capture, beneficial if there is no N_2 in flue gas

Oxy-combustion



- Excluding N_2 gives ~70% less flue gas
- T_{ad} 2500+ °C
- Recirculating part of flue gas lowers gas T

Oxy-combustion - recovery boiler chemistry

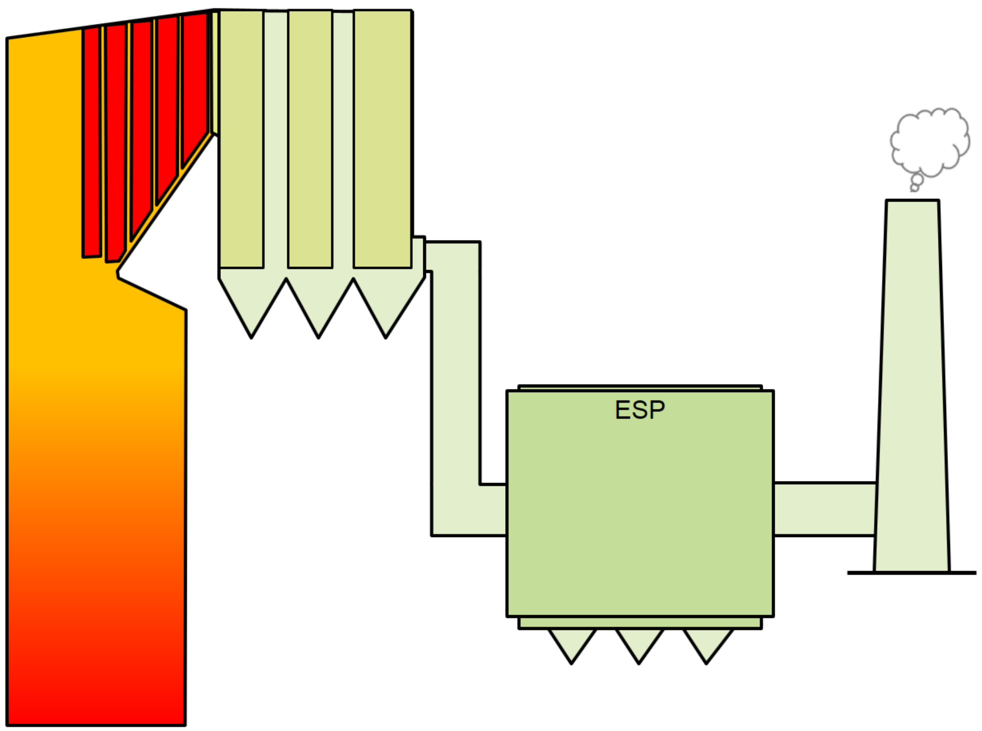
”Air-firing”:

- $O_2 + N_2$ introduced into boiler as oxidizer

”Oxy-firing”:

- $O_2 + CO_2$ (+H_2O)

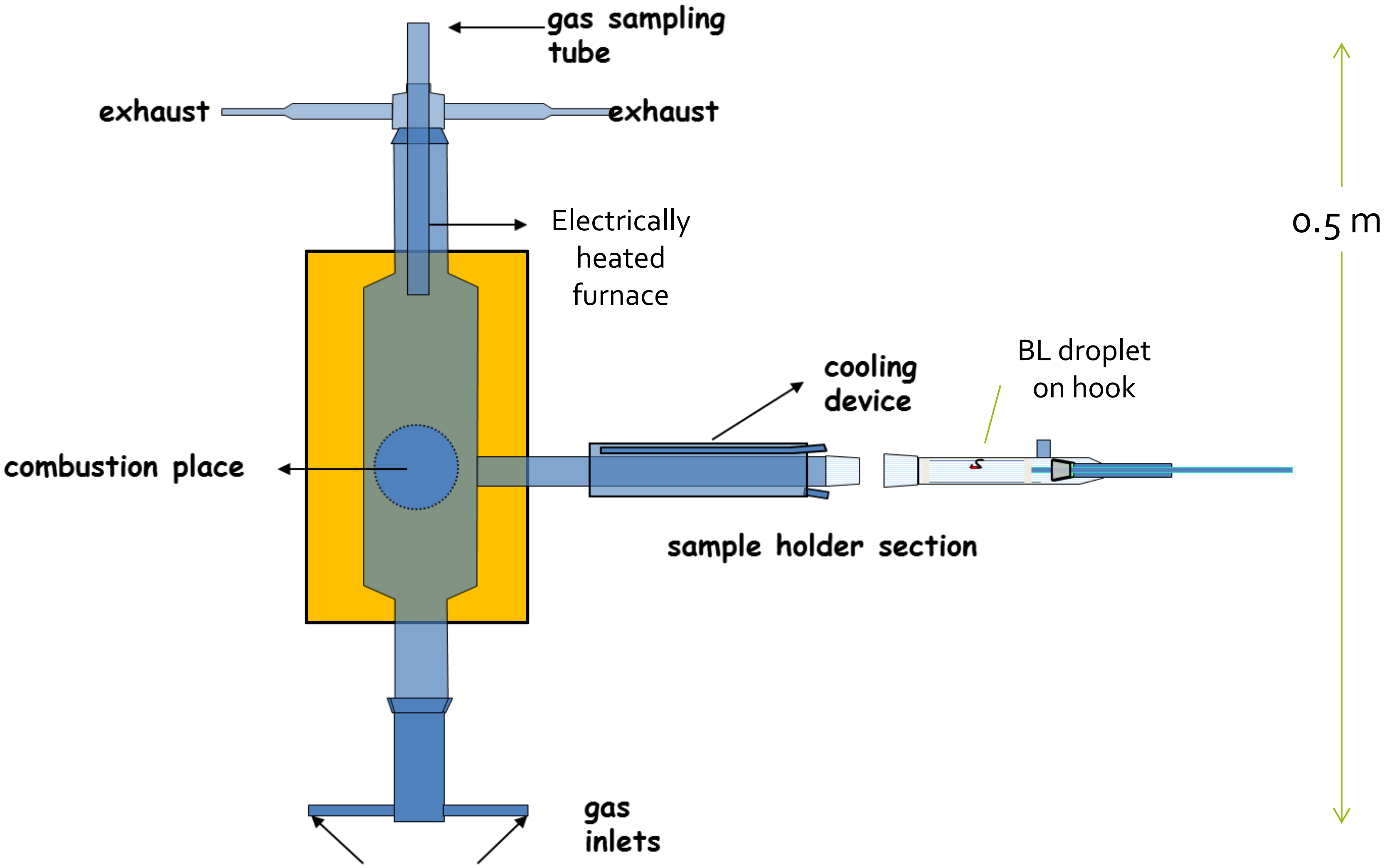
- CO_2 and H_2O concentrations higher (also $CO + H_2$)
- Impacts?
  - Black liquor burning (gasification reactions)
  - Char oxidation kinetics
  - Char bed burning and sulfur reduction
  - Element release, fume and emission formation
  - Fouling, corrosion
  - Heat transfer (radiation, convection)
  - …



Single droplet studies

- Controlled
  - Reactor temperature
  - Reactor gas composition
- Combustion video
  - Swelling
  - Burning times
- Emissions –gas analysis
  - CO, CO_2, SO_2, NO
- Smelt / residue analysis
  - Amount, composition

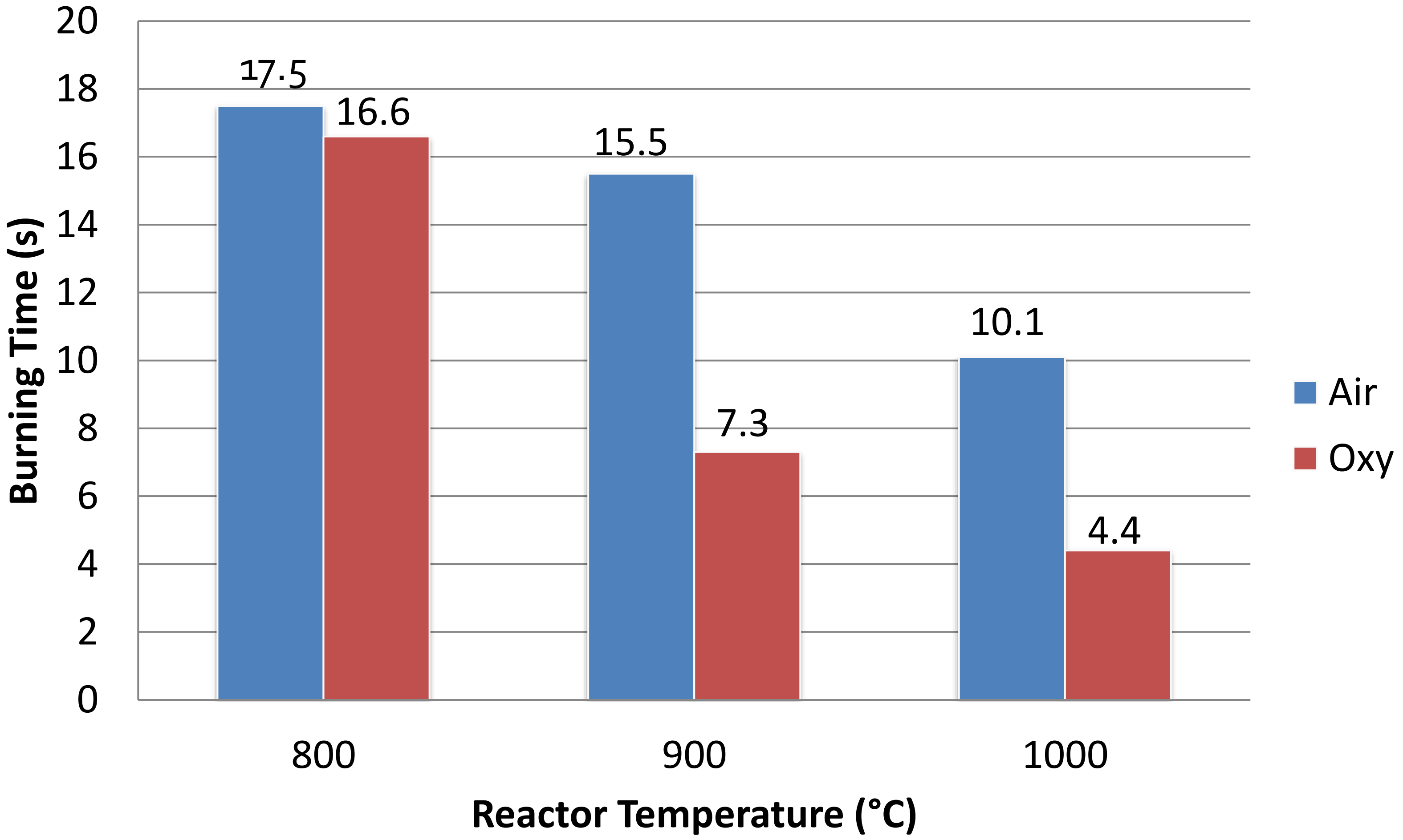
ÅA single droplet reactor



Combustion experiments

- Three different liquors (75-80 %DS)
  - Spain, hardwood (BL623)
  - Nordic, softwood (BL624)
  - USA, softwood (BL626)
- Video recorded combustion experiments in the single particle reactor (SPR) with gas analyzers
- Sets of six droplets (10-11 mg)
- Reactor temperature 800℃, 900℃, 1000℃
- Oxidizer mixtures
  - 3 vol-% O_2 / 97 vol-% N_2 (”Air”)
  - 3 vol-% O_2 / 97 vol-% CO_2 (”Oxy”)

Burning times



Objective

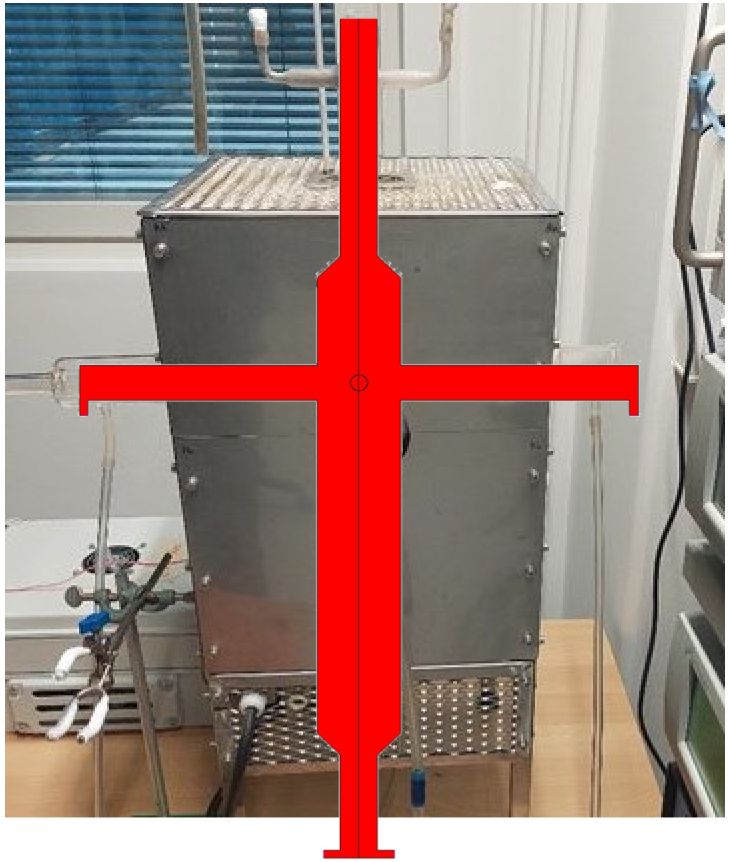
- Better understanding of heat and mass transfer in single droplet experiments relevant for black liquor oxy-combustion
- Leverage this understanding to interpret and support experimental results

CFD modeling of single droplet experiments

- Case setup: 2D simulation of the Åbo Akademi single particle reactor
- oxidizer mixtures
  - 3 vol-% O_2 / 97 vol-% N_2 (”Air”)
  - 3 vol-% O_2 / 97 vol-% CO_2 (”Oxy”)
- A 5 mm radius char particle
- Reactor temperature 800℃,900℃,1000℃
- The models used; energy equation, viscous model (laminar), radiation model (Discrete Ordinates), species transport

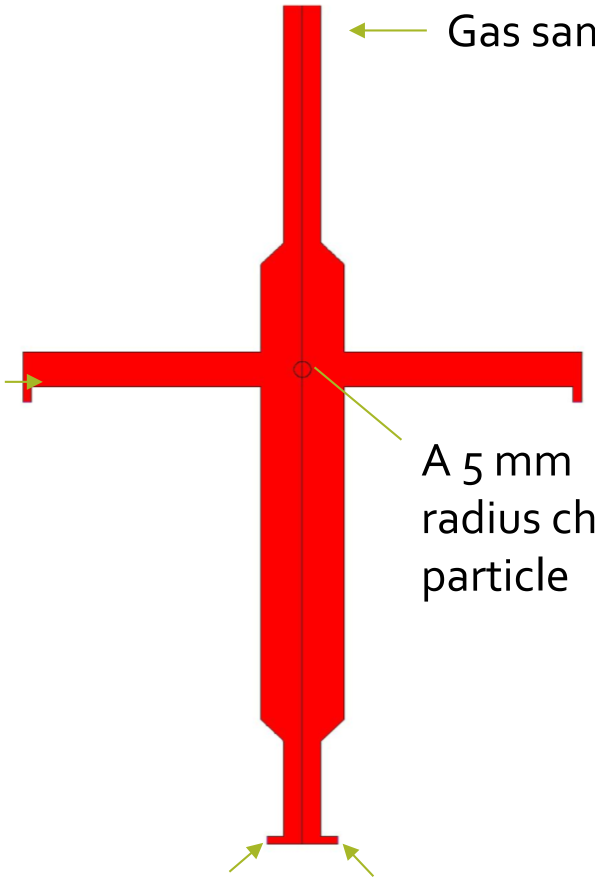
CFD modeling of single droplet experiments

- Case setup: 2D simulation of the Åbo Akademi single particle reactor



CFD modeling of single droplet experiments

- Case setup: 2D simulation of the Åbo Akademi single particle reactor



Thermal analysis

- Reactor temperature 800°C, 900°C, 1000°C
- Gas is introduced into the reactor at room temperature
- Research questions
  - What is the temperature of the gas that reaches the particle ?
  - What is the temperature the particle reaches at steady-state ?
  - What is the role of radiative heat transfer ?

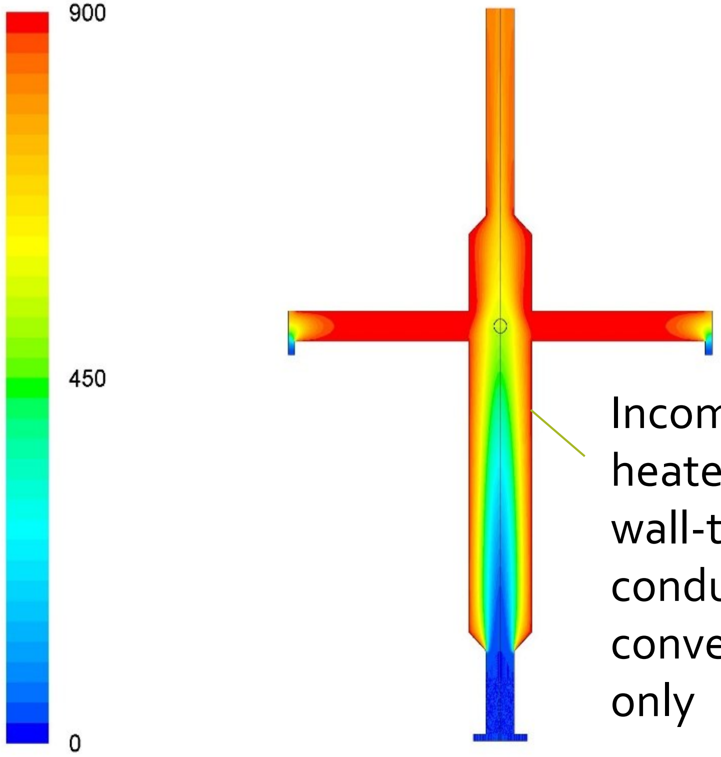
- To test, simulate both (air / oxy) cases with radiation on / off

Results

- Reactor temperature 900℃

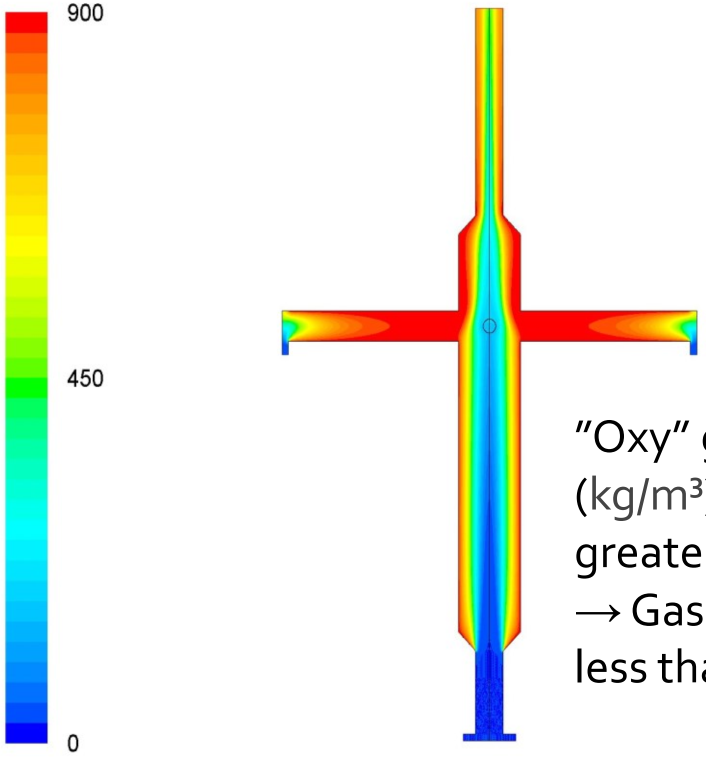
Temperature (No radiation)

Air
3% O_2 / 97% N_2



Incoming gas heated by wall-to-gas conduction/ convection only

Oxy
3% O_2 / 97% CO_2

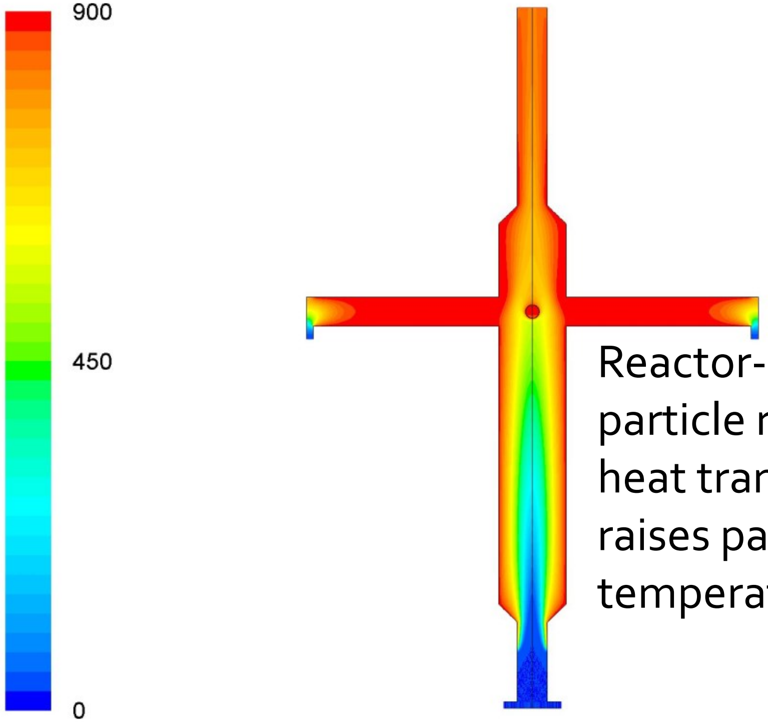


"Oxy" gas density (kg/m³) is 55% greater
→ Gas heats up less than "Air" gas

Temperature (Surface-to-surface(S2S) radiation on)

Air

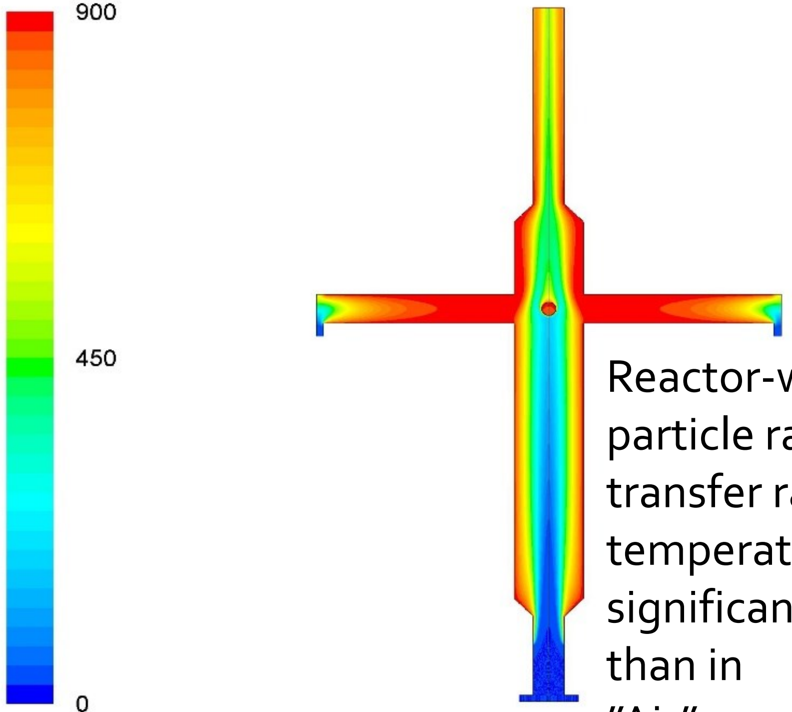
3% O_2 / 97% N_2



Reactor-wall-to-particle radiative heat transfer raises particle temperature

Oxy

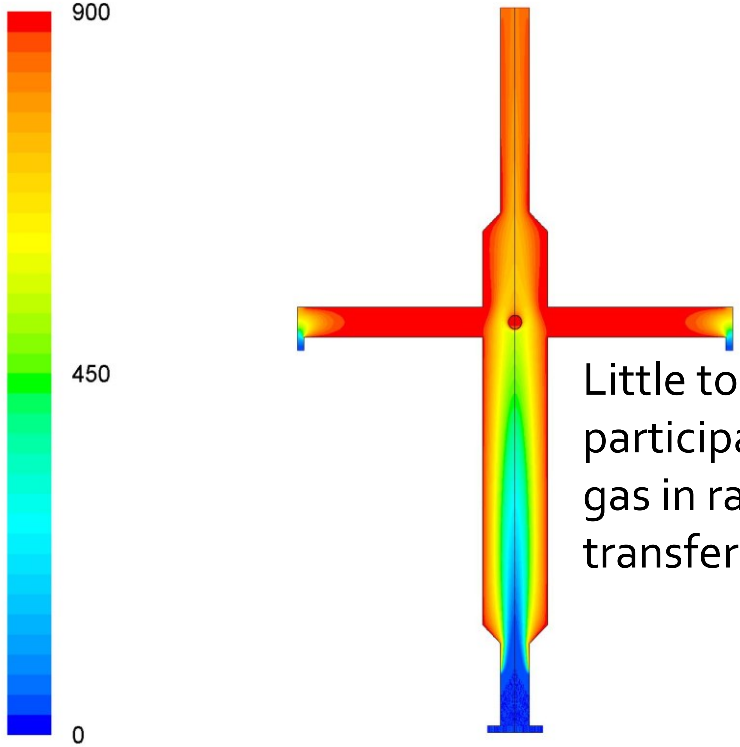
3% O_2 / 97% CO_2



Reactor-wall-to-particle radiative heat transfer raises particle temperature significantly; more than in "Air" case

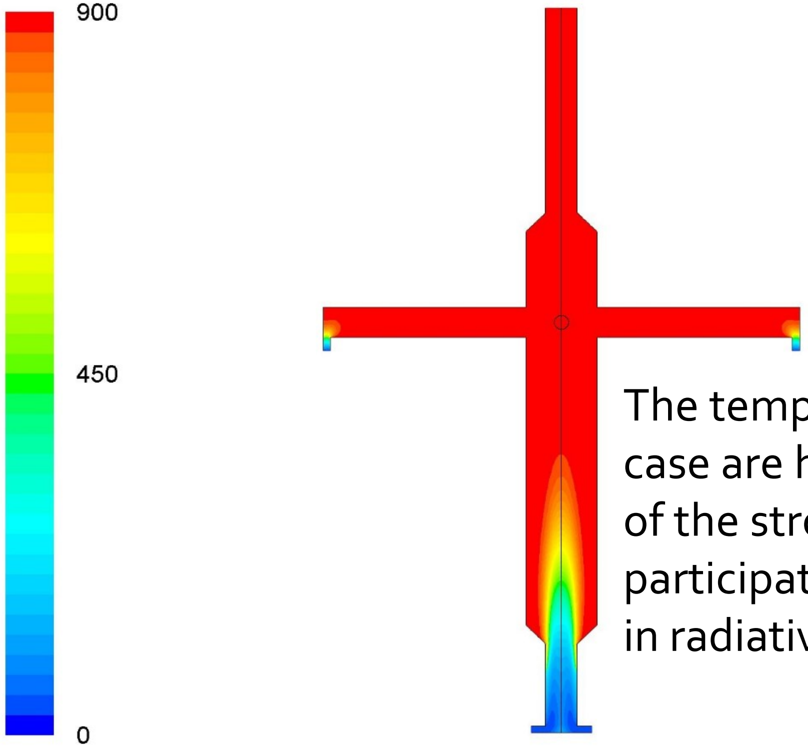
Temperature (S2S and gas radiation on)

Air
3% O_2 / 97% N_2



Little to no participation of air gas in radiative heat transfer

Oxy
3% O_2 / 97% CO_2



The temperatures in oxy case are higher because of the stronger participation of the gas in radiative heat transfer

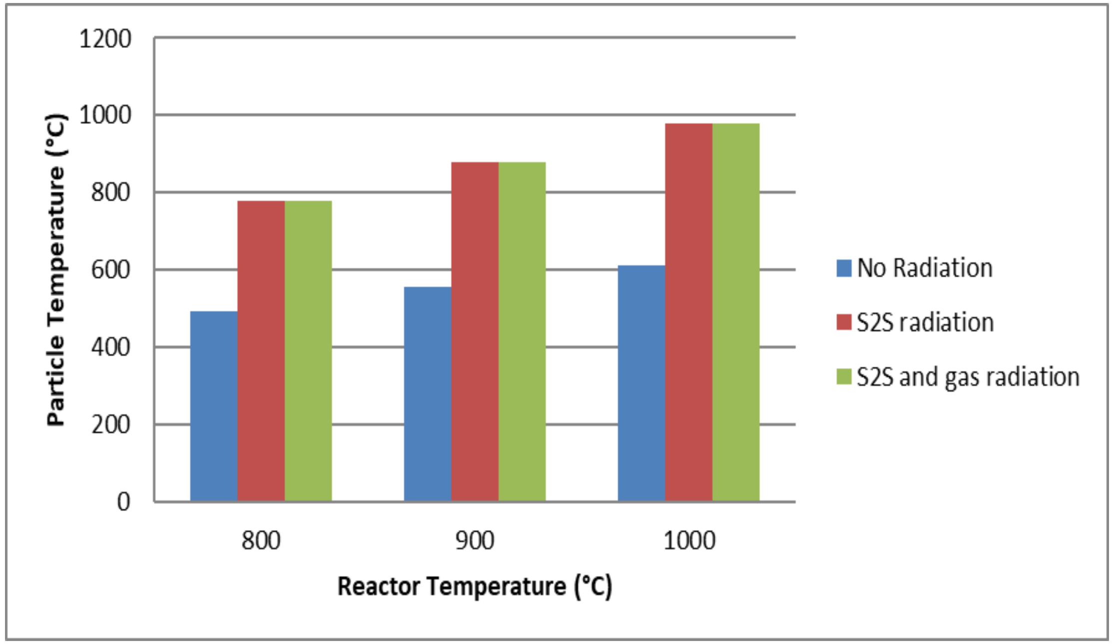
CFD modeling at 800 and 1000℃

- Both gases behave similarly under different radiation scenarios at 800–1000 ℃
- Particle temperature increases with the rising reactor temperature

Particle temperature vs reactor temperature

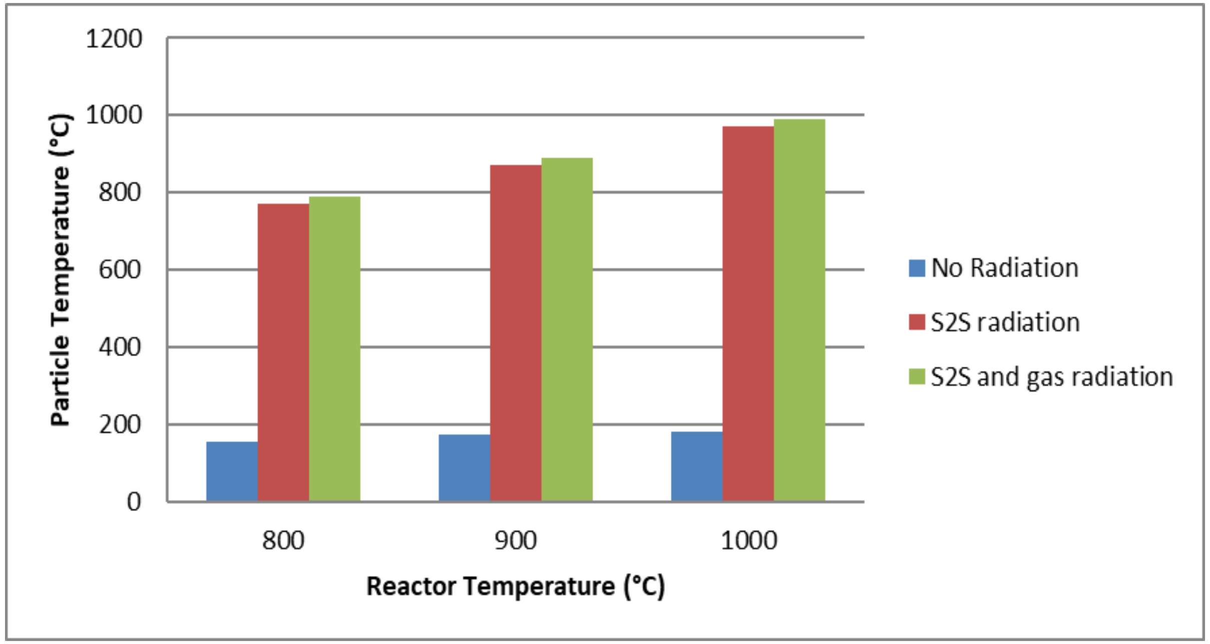
Air

3% O_2 / 97% N_2



Oxy

3% O_2 / 97% CO_2



*S2S: Surface to surface

Summary

Reactor Temperature ℃	Particle Temperature ℃					
	No radiation		S2S radiation		S2S and gas radiation	
	Air	Oxy	Air	Oxy	**Air**	**Oxy**
800	493	155	780	769	**780**	**791**
900	554	174	880	870	**880**	**890**
1000	612	182	980	972	**980**	**989**

Continued.

Without Radiation:

- Heat transfer by convection only, less effective than radiation
- Particle much cooler than reactor
- Oxy case shows a greater deviation from reactor temperature
- With the Oxy case, the mass flow of gas is 55% greater
- Greater mass flow is heated up to lesser extent than Air gas

With Radiation:

- Steady state particle temperature significantly higher, approaching reactor temperature
- Heat transfer is enhanced by radiation
- Effect is stronger in oxy case due to CO_2's high radiative absorption

Char burning analysis

- Research questions
  - What is the role of char carbon CO_2 gasification in droplet conversion?
  - What are droplet burning times based on Char-C mass conversion rate and droplet radius decrease rate?
  - To what extent do the modeled burn times agree with the experimental data?

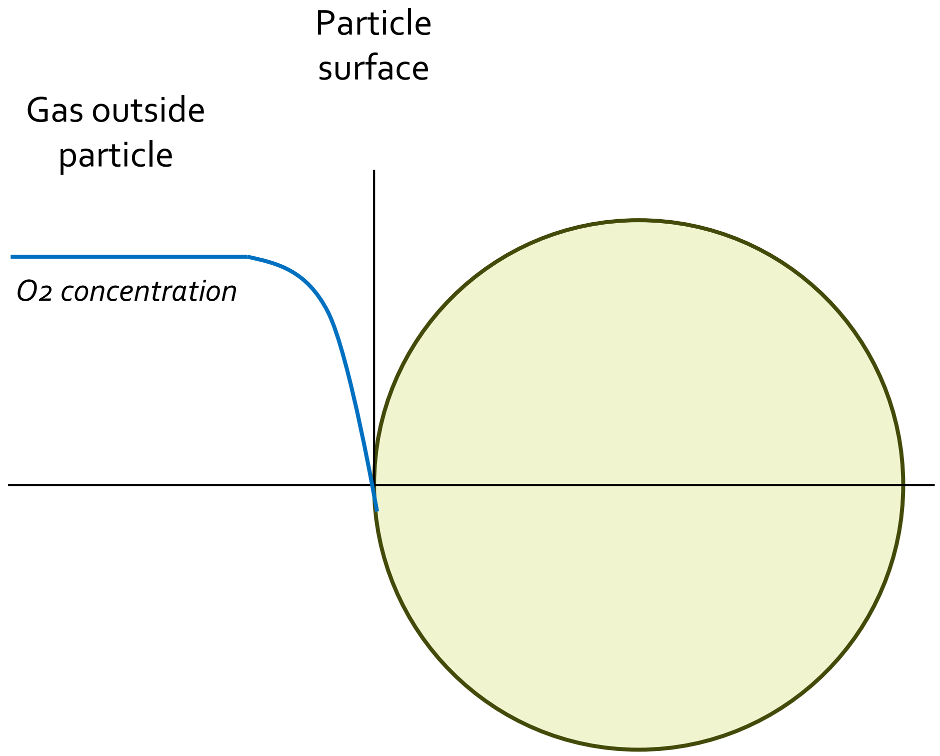
Char burning analysis

- Reactor temperature 800℃, 900℃, 1000℃
- Reactor-wall-to-particle-surface and reactor-wall-to-gas Radiation on
- Char reaction type
  - External mass transfer limited
  - Char reaction kinetics using finite rates
- Simulate both (air / oxy) cases with radiation on

Char reactions

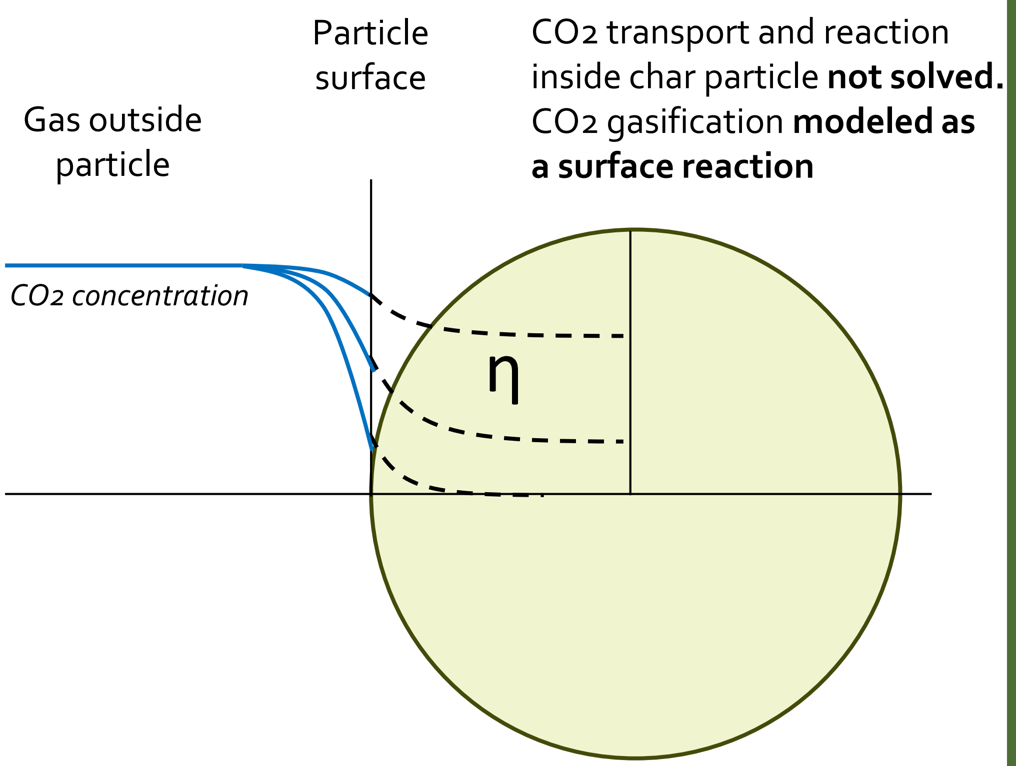
- Char-C reactions involving gas species

- Char-C + O_2 (external mass transfer limited)
  - $2C + O_2 \rightarrow 2CO$



Char reactions

- Char-C reactions involving gas species
- Char-C + O_2 (external mass transfer limited)
  - $2C + O_2 \rightarrow 2CO$
- **Char-C + CO_2 (Char reaction kinetics using finite rates)**
  - $C + CO_2 \rightarrow 2CO$
- Kinetic parameters used in calculation (Li and van Heiningen)
- CO2 gasification rate in char particle estimated using efficiency factor (η)



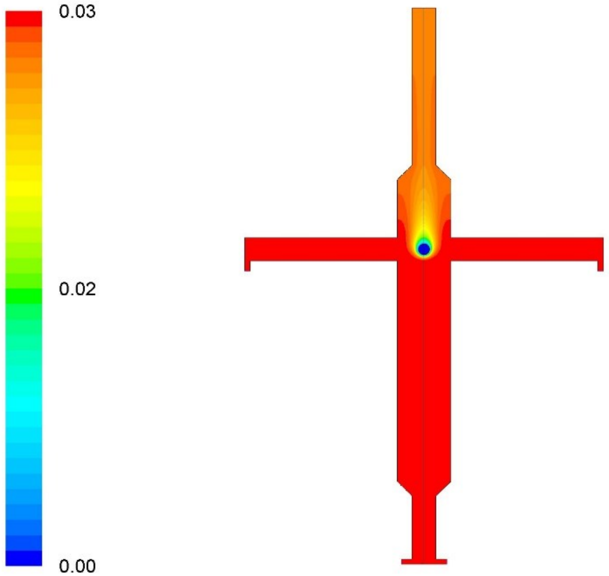
Results

- Reactor temperature 900℃

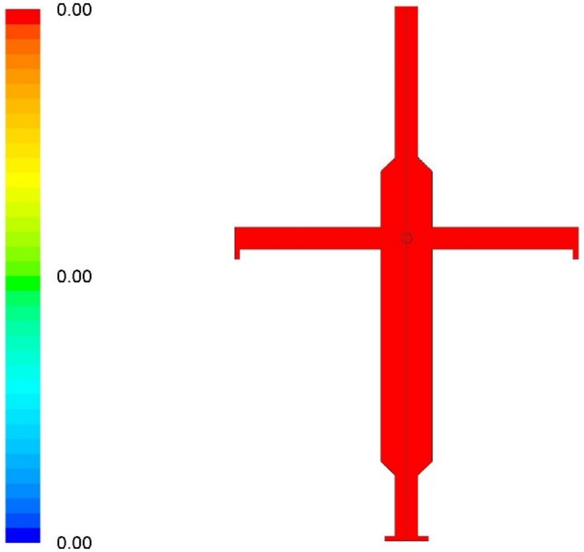
Char reactions-Air

Air
3% O_2 / 97% N_2

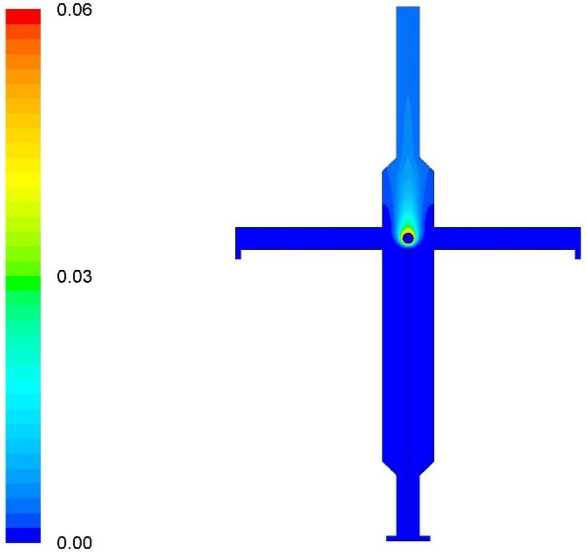
Mole fraction of O_2



Mole fraction of CO_2



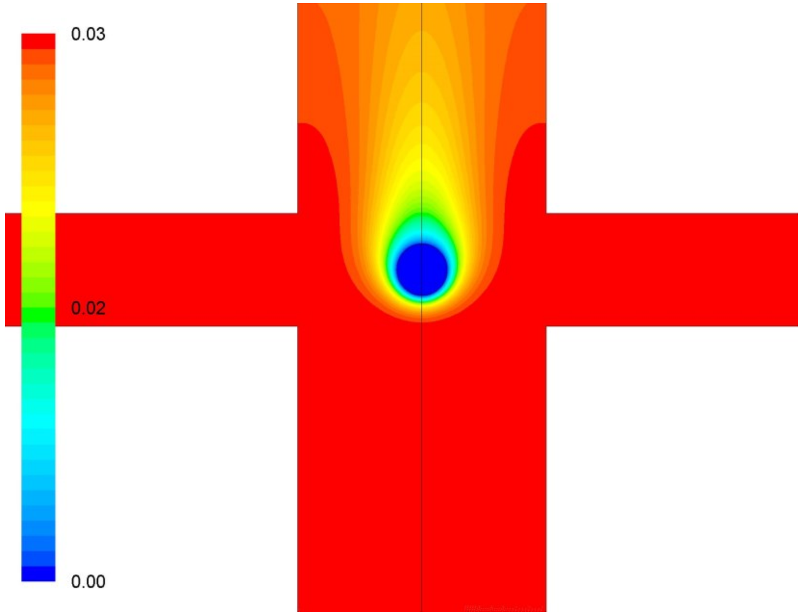
Mole fraction of CO



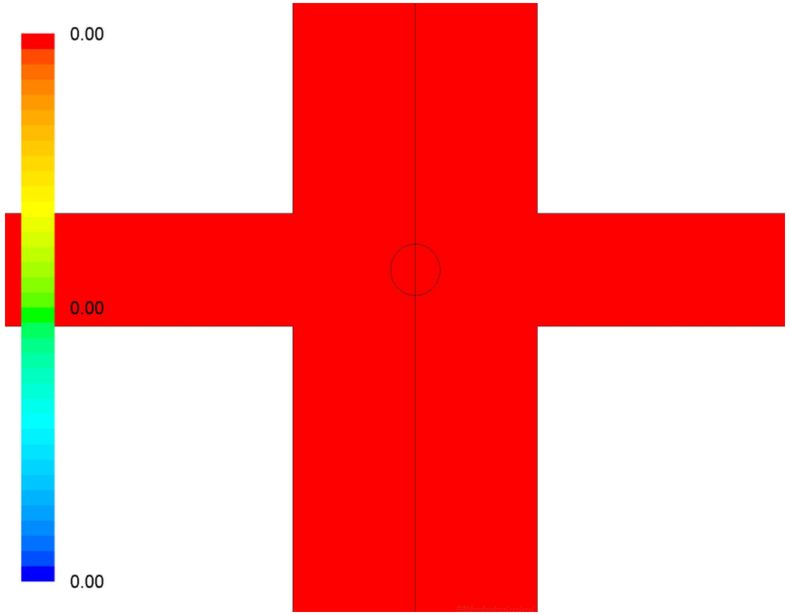
Air

$3\%\ O_2\ /\ 97\%\ N_2$

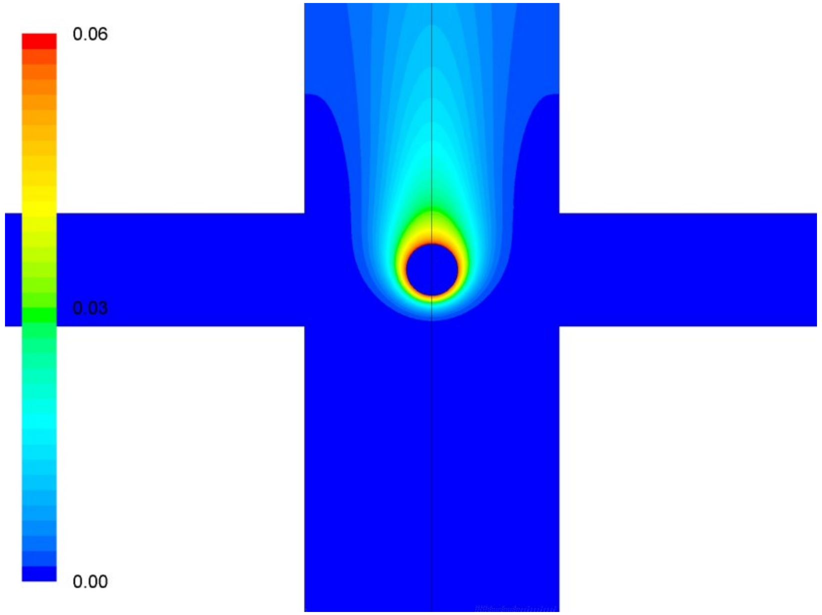
Mole fraction of O_2



Mole fraction of CO_2



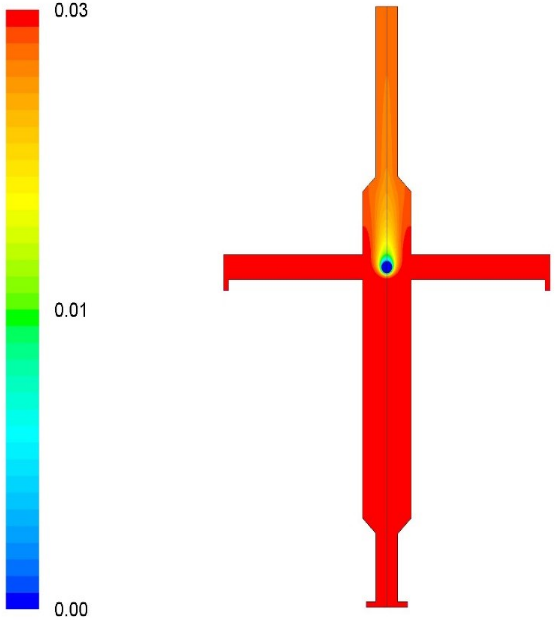
Mole fraction of CO



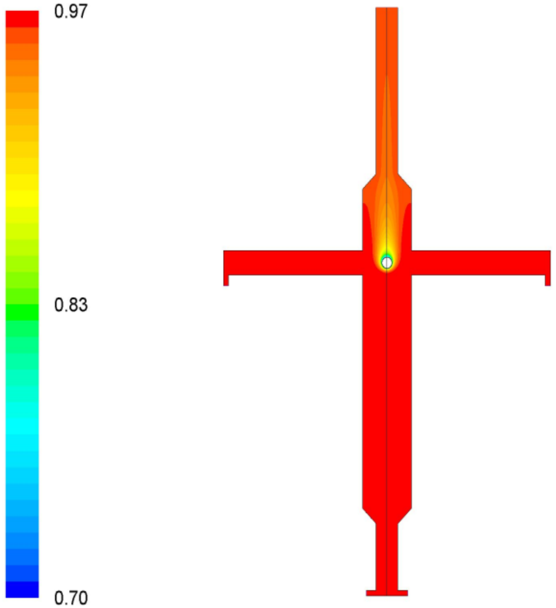
Char reactions-Oxy

Oxy
3% O_2 / 97% CO_2

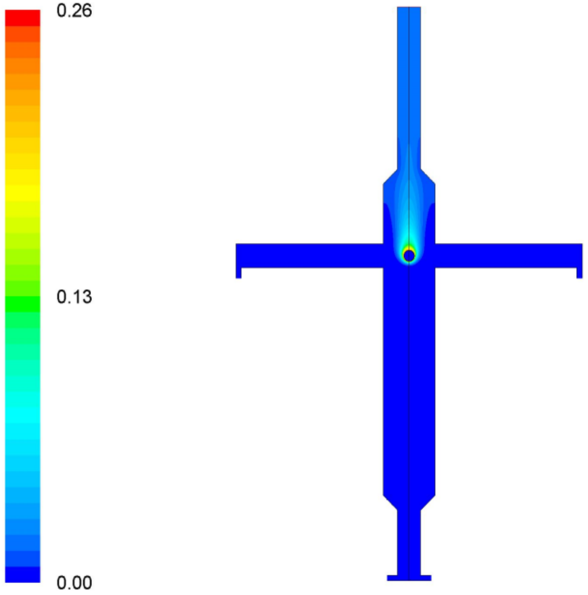
Mole fraction of O_2



Mole fraction of CO_2



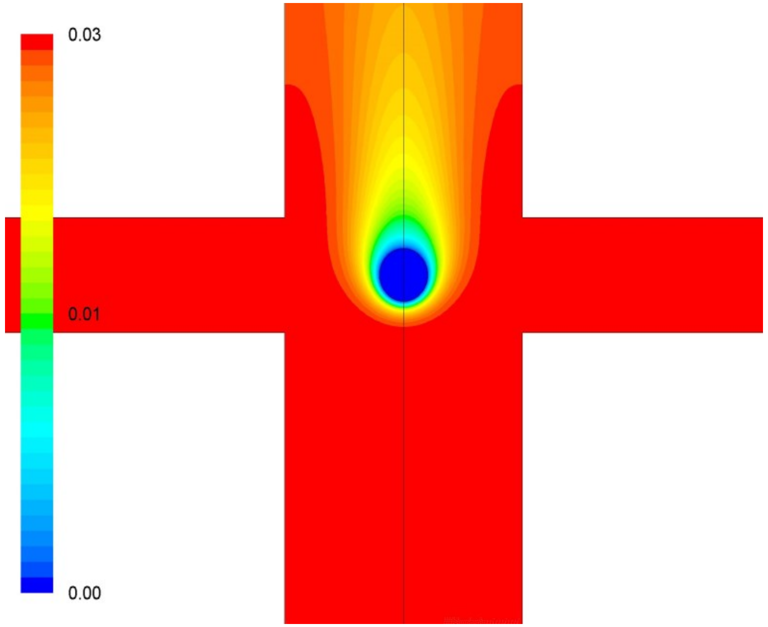
Mole fraction of CO



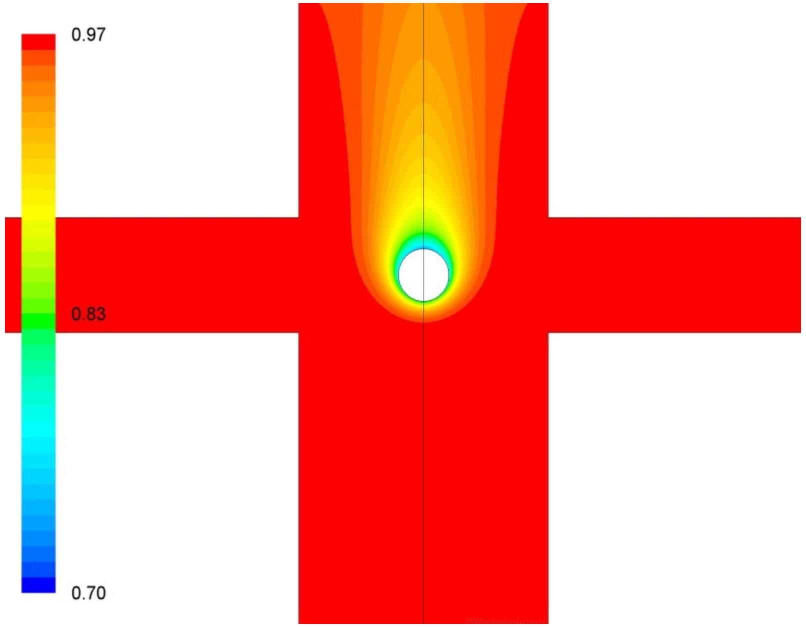
Oxy

$3\%\ O_2\ /\ 97\%\ CO_2$

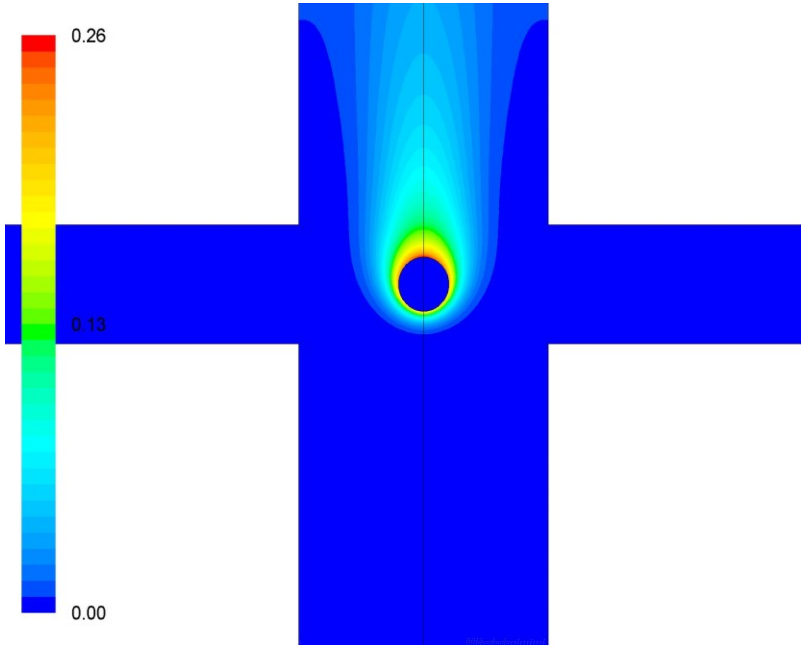
Mole fraction of O_2



Mole fraction of CO_2



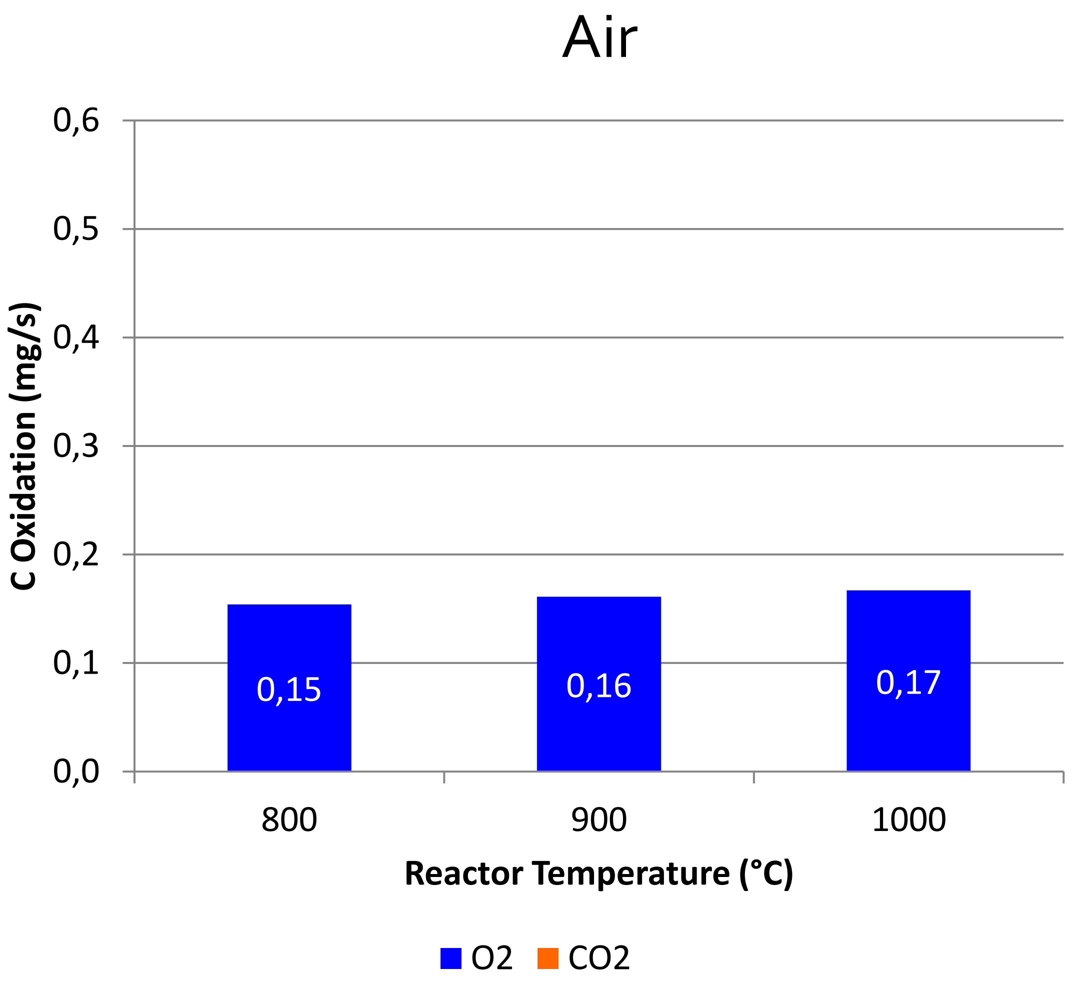
Mole fraction of CO

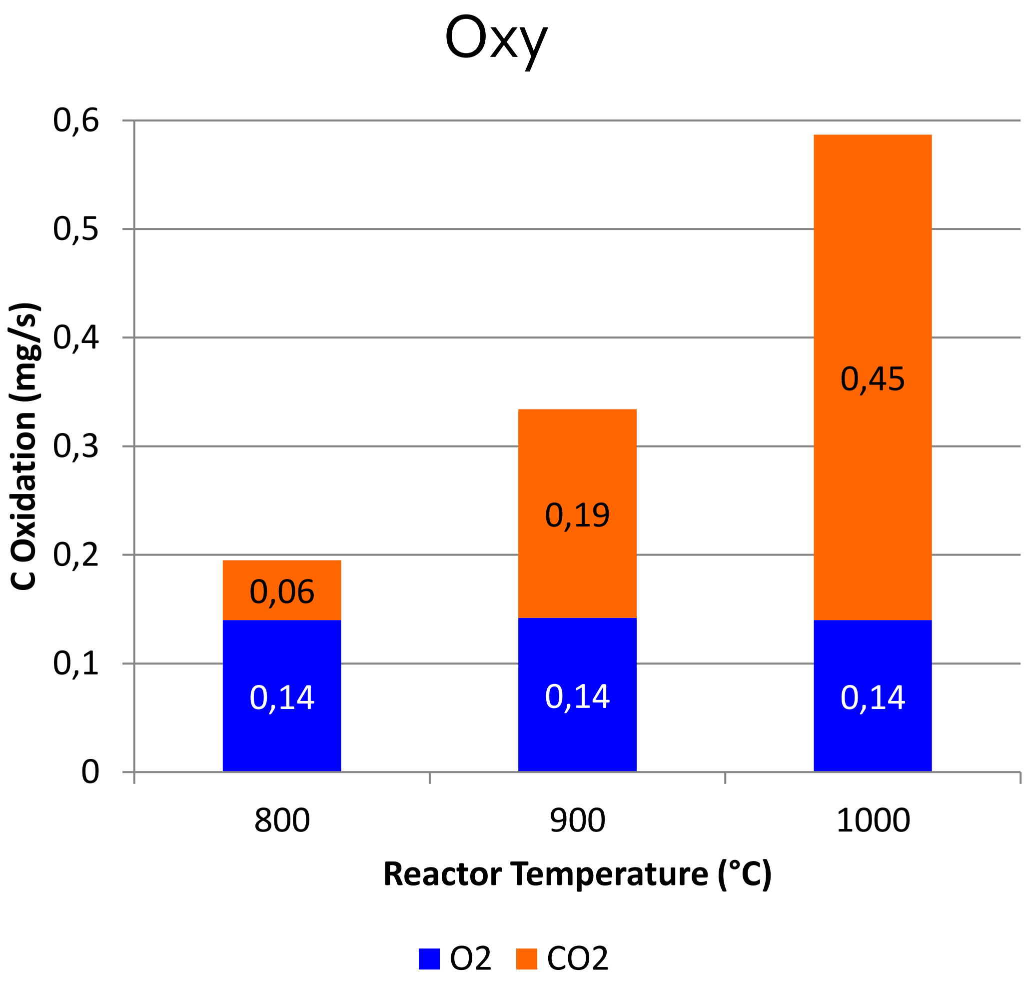


Char-C oxidation

- In air case, Char-C oxidized by O_2, no involvement of CO_2
- In Oxy case, Char-C oxidized by O_2, CO_2
  - Involvement of CO_2 in char oxidation results in more CO production

Char-C oxidation





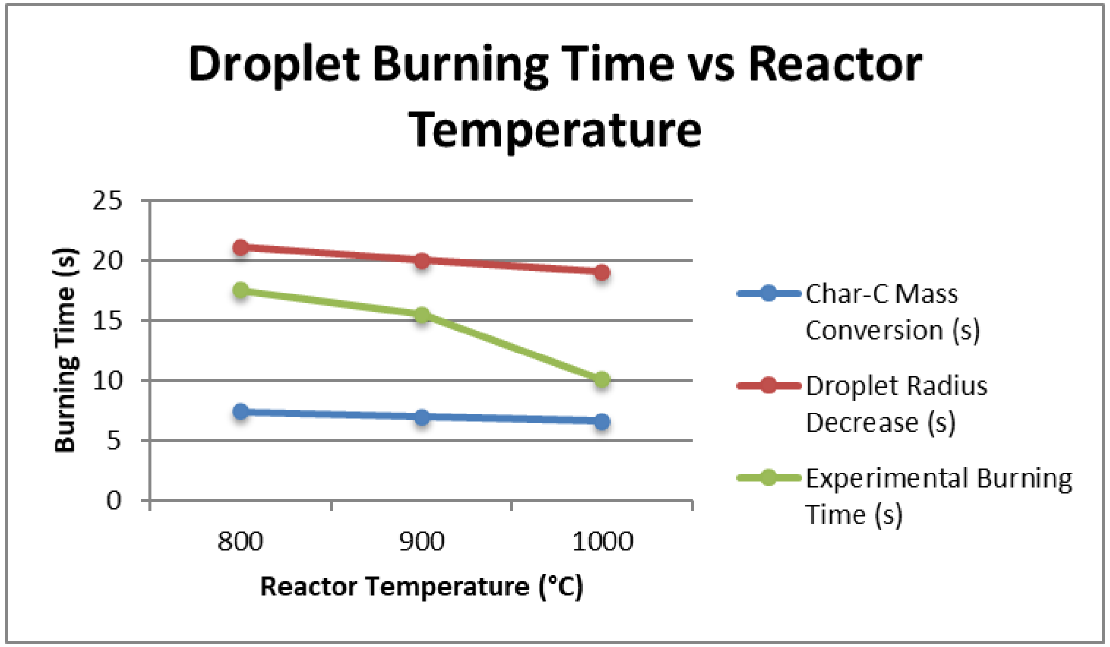
Droplet burning times (s)

- Droplet burning times estimated based on:
- Char-C mass conversion rate
  - Mass conversion rate assumed constant
  - Droplet char-C per char-C oxidation rate
- Droplet radius decrease rate
  - Mass flux assumed constant
  - Initial droplet radius per droplet radius decrease rate
  - radius decrease rate estimated from char-C volume consumption

Burning times (s)

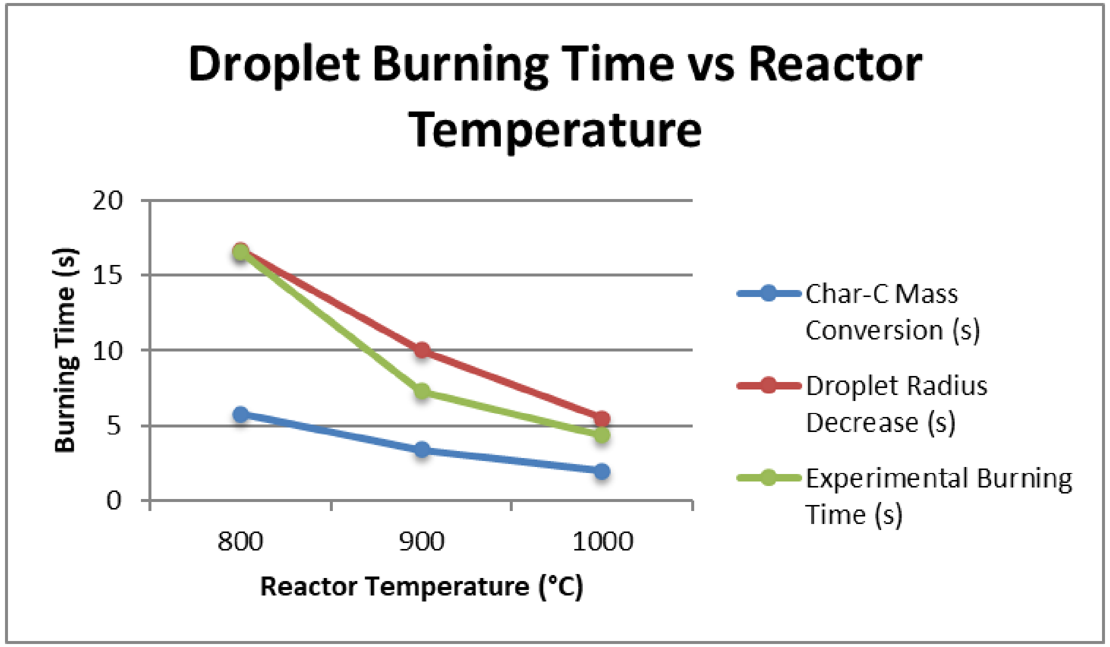
	Air			Oxy		
Reactor temperature °C	800	900	1000	800	900	1000
Droplet burning time based on						
Char-C mass conversion rate (s)	7.4	7.0	6.6	5.8	3.4	2
Droplet radius decrease rate (s)	21.1	20	19	16.7	10	5.5

Air



Droplet Burning Time vs Reactor Temperature
Burning Time (s)
25
20
15
10
5
0
800
900
1000
Reactor Temperature (°C)
Char-C Mass Conversion (s)
Droplet Radius Decrease (s)
Experimental Burning Time (s)

Oxy



Droplet Burning Time vs Reactor Temperature
Burning Time (s)
20
15
10
5
0
800
900
1000
Reactor Temperature (°C)
Char-C Mass Conversion (s)
Droplet Radius Decrease (s)
Experimental Burning Time (s)

Summary and conclusions

- Char oxidation in single droplet experiments modeled using CFD
- Radiation key factor in droplet heat-up and steady-state temperature
- Insights gained into contributions of O_2 and CO_2 in char carbon oxidation in reactor conditions ”air” and ”oxy”
- Future work includes
  - Adding char reactions (H_2O, Na_2CO_3, Na_2SO_4 -Na_2S)
  - Extend model by solving transport and reactions inside char particle
  - Transient model to describe time-dependent char oxidation

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