The Clean Energy Transition Partnership

Thermodynamic and practical aspects of oxyfuel CO_2 capture strategies for kraft recovery boilers

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Oxy-Kraft

Oxy-fired black liquor recovery boiler

Introduction – Pulp mills as BECCS

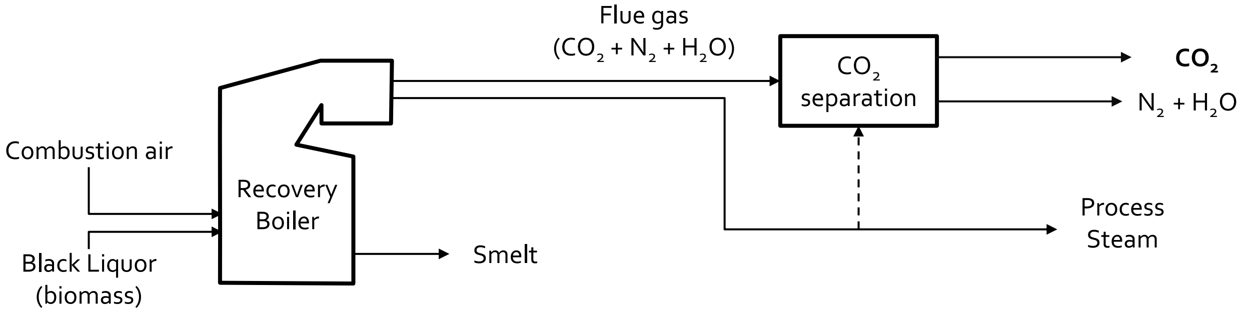
- Pulp and paper industries (PPI) represent a source of biogenic CO_2 emissions
  - Ca. 92 Mt-CO_2/y in Europe [1], 101 Mt-CO_2/y in USA [2]
- Sequestering biogenic CO_2 from PPI can provide net-negative emissions as a BECCS system.
  - ~150-1200 Gt-CO_2 forecast for BECCS removal by 2100 [3]
  - ~2.5-20 Gt/y over 2040-2100

Biogenic CO_2 emissions from PPI sites [4]

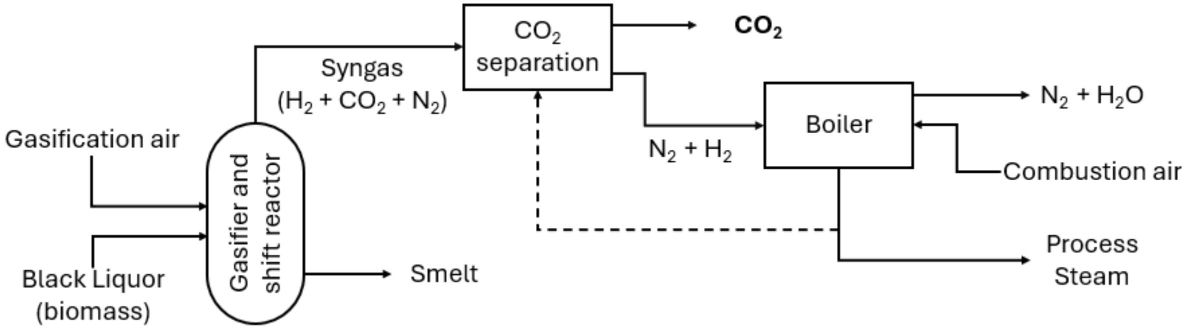
[1] Lipiäinen et al. (2023)
[2] US EPA (2022)
[3] IPCC (2018)
[4] Endrava (2024)

Introduction – CCS processes

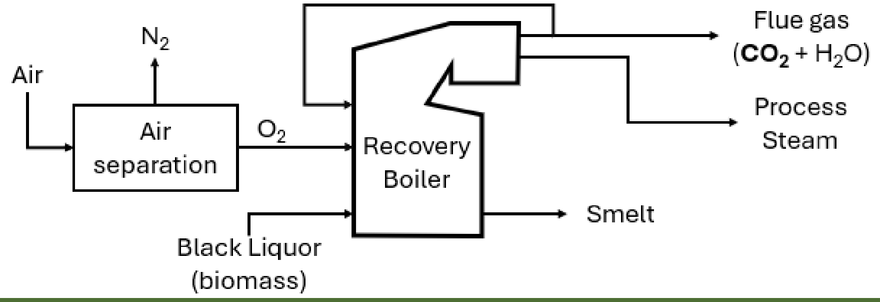
- Post-Combustion



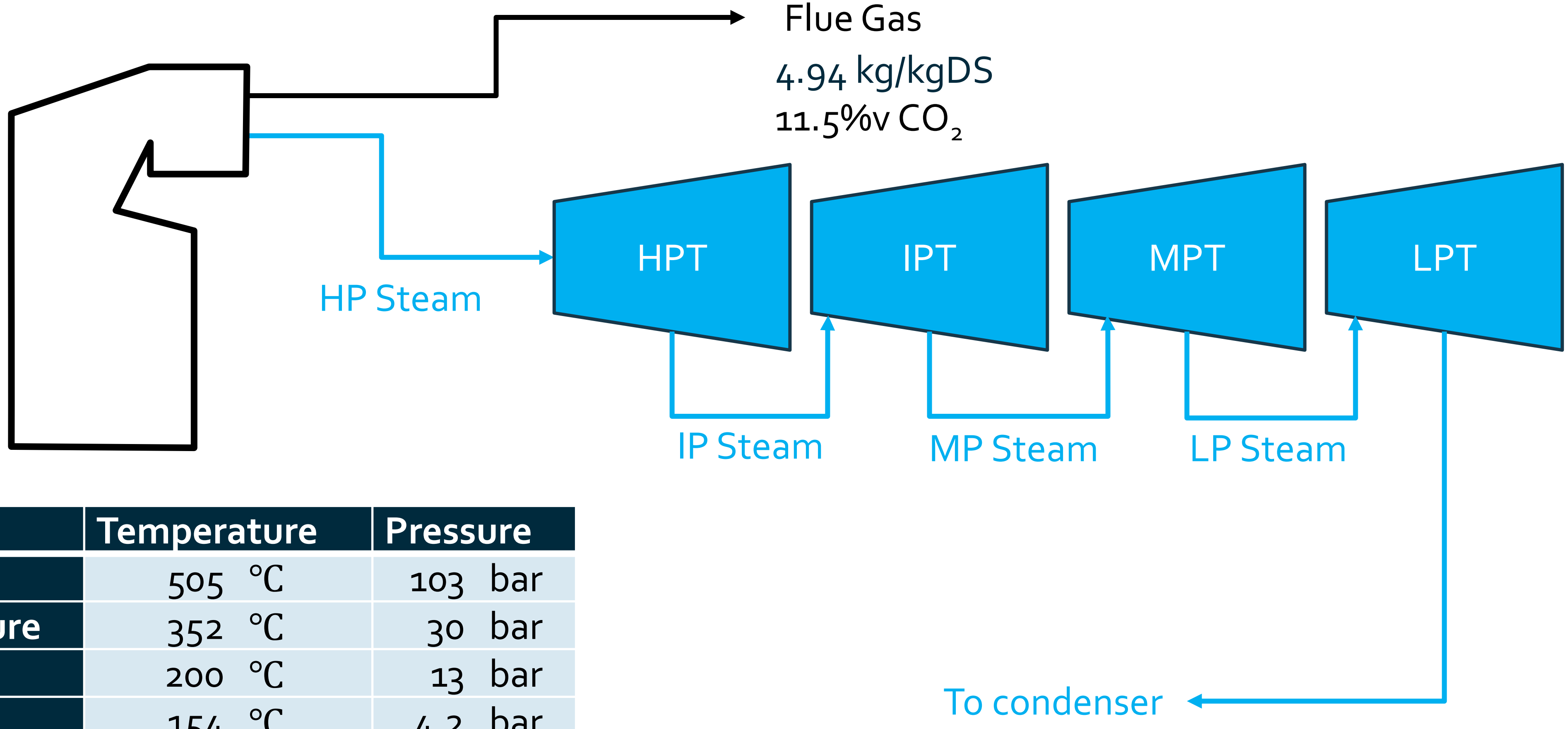
- Pre-Combustion



- Oxyfuel Combustion

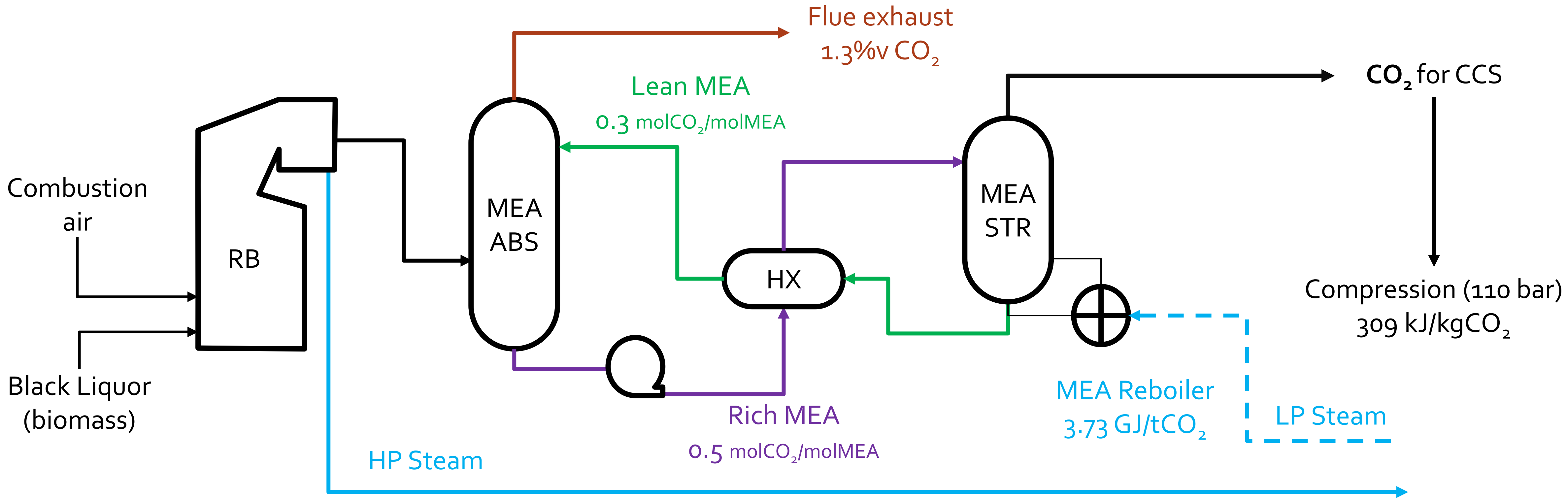


Reference Recovery Boiler

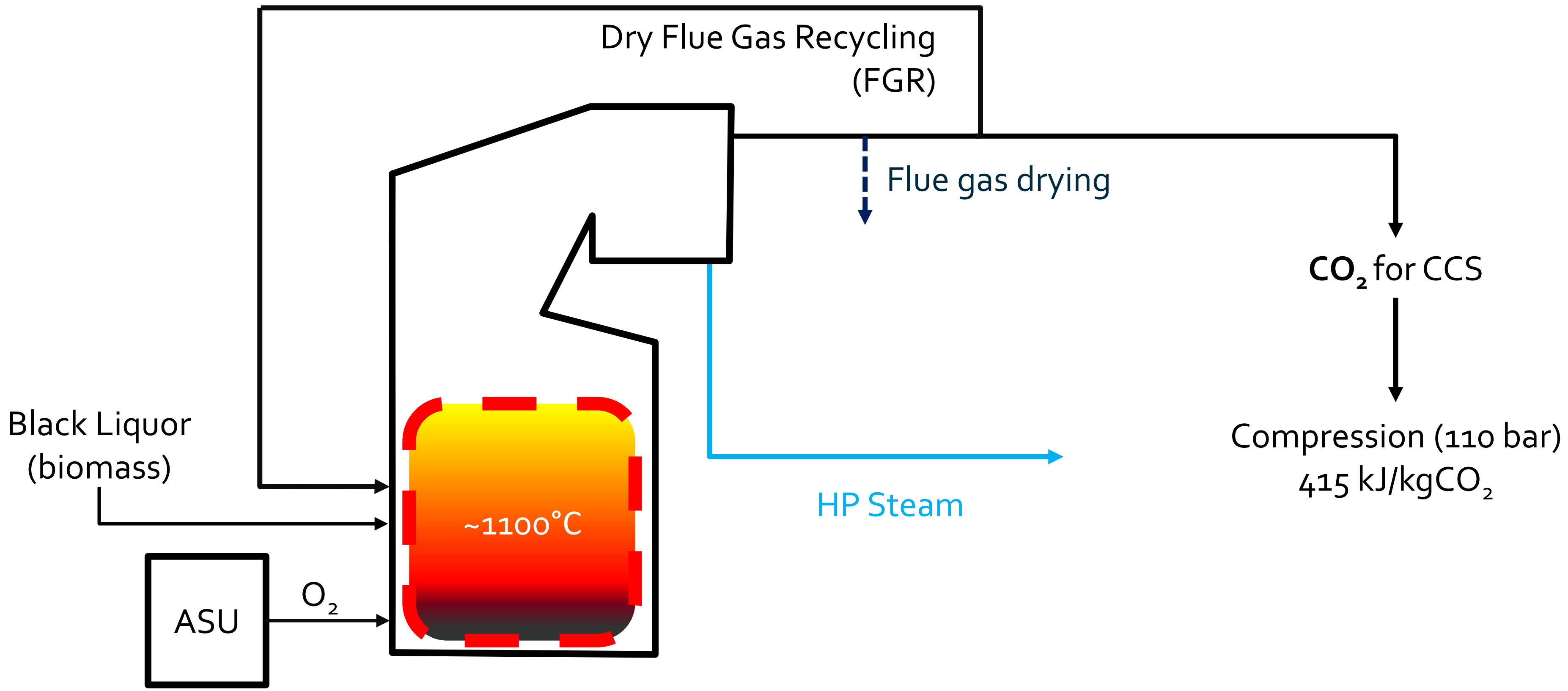


Steam Properties	Temperature	Pressure
High pressure	505 °C	103 bar
Intermediate pressure	352 °C	30 bar
Medium pressure	200 °C	13 bar
Low pressure	154 °C	4.2 bar

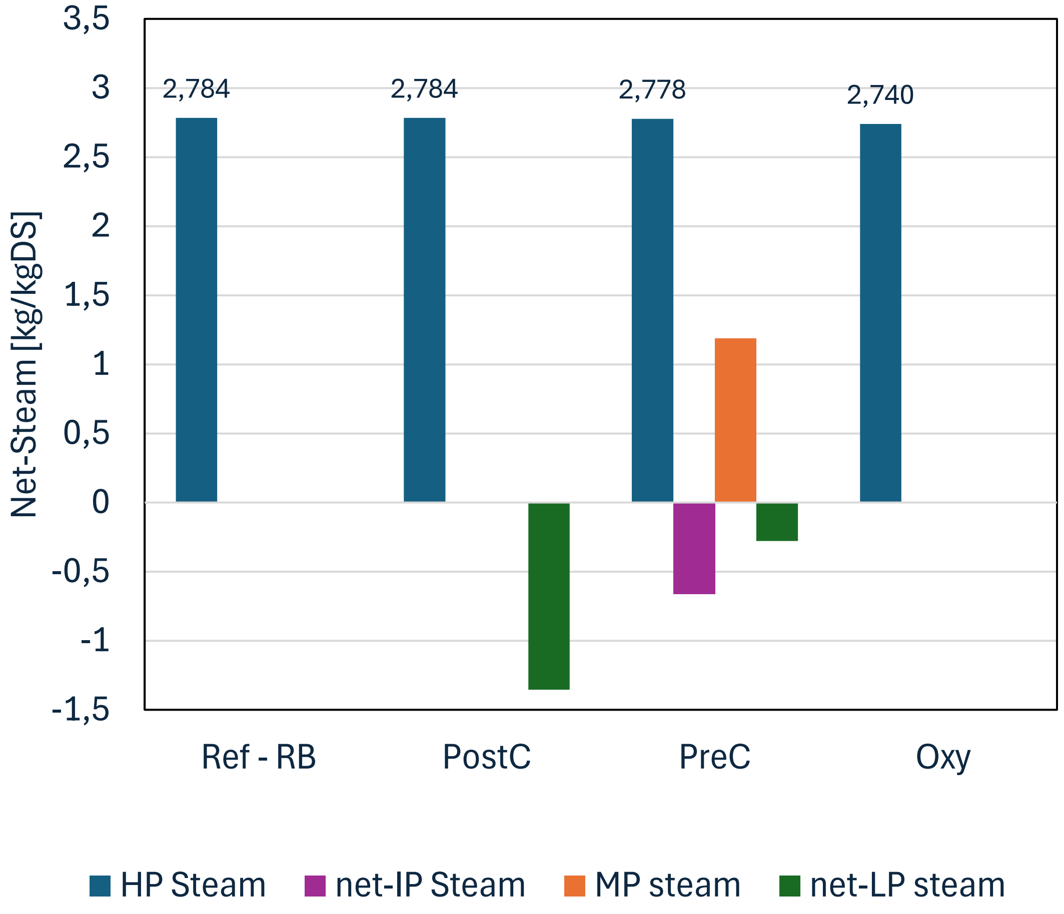
Post-combustion (PostC)

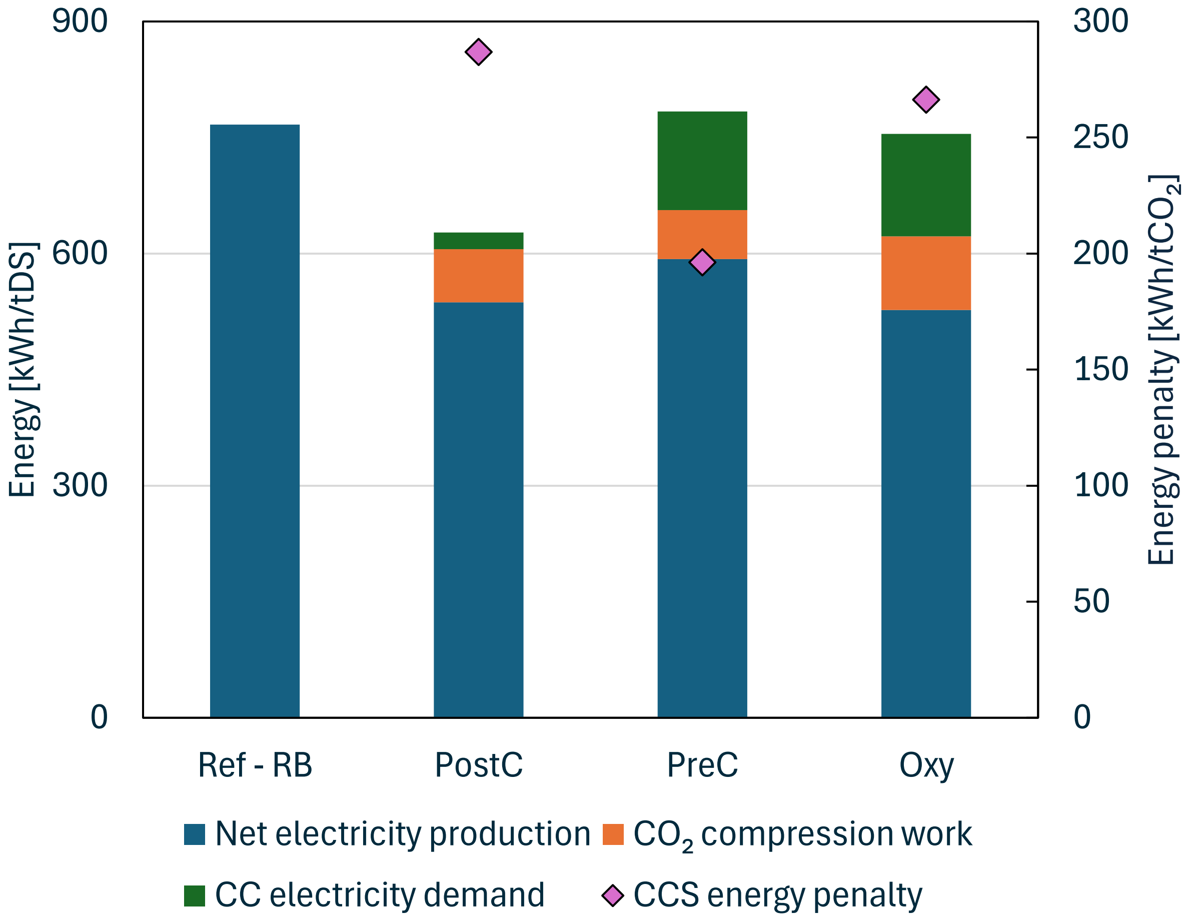


Oxyfuel combustion (Oxy)



CCS processes

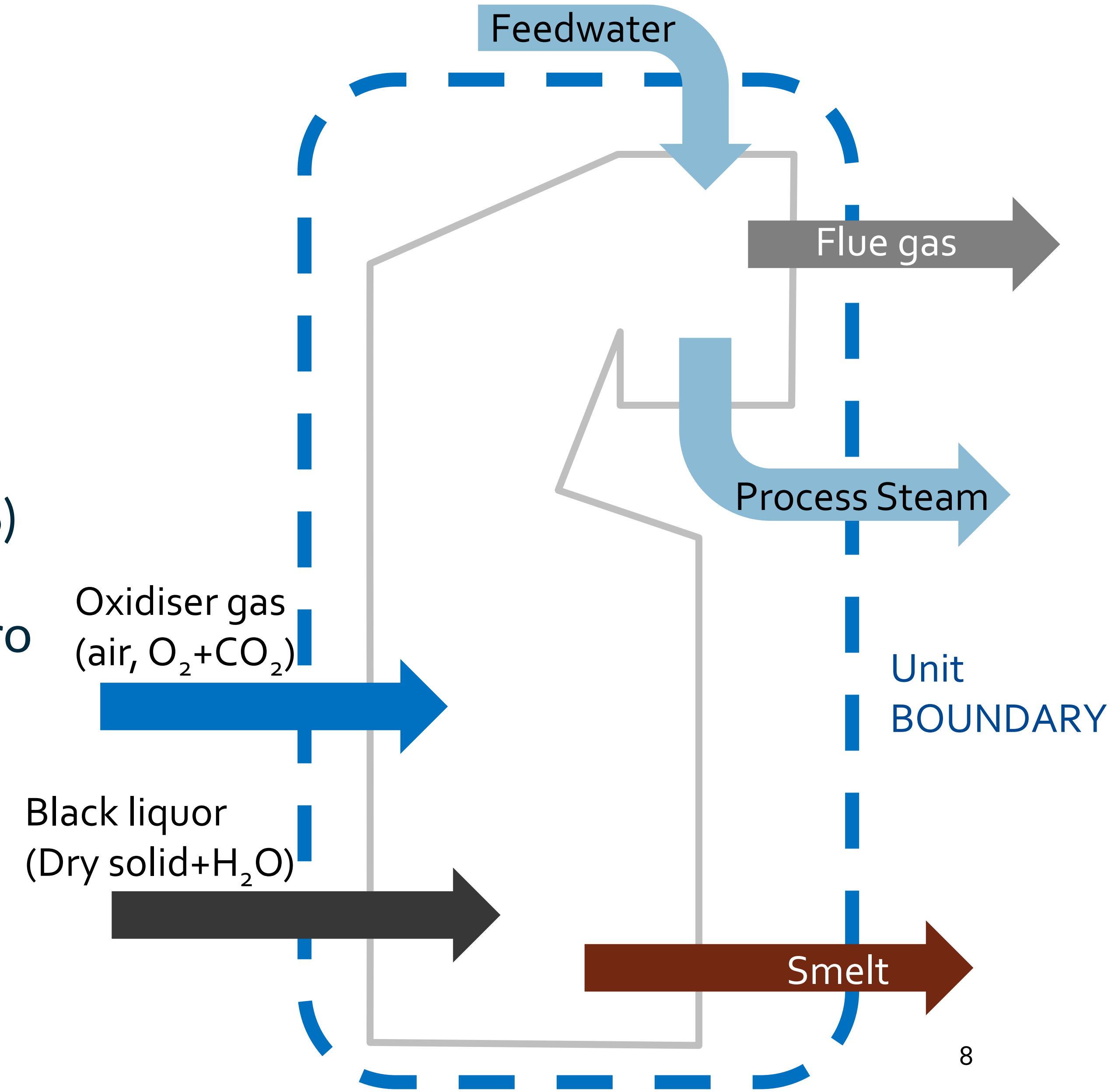




[5] Greencorn et al. (2025)

Methodology

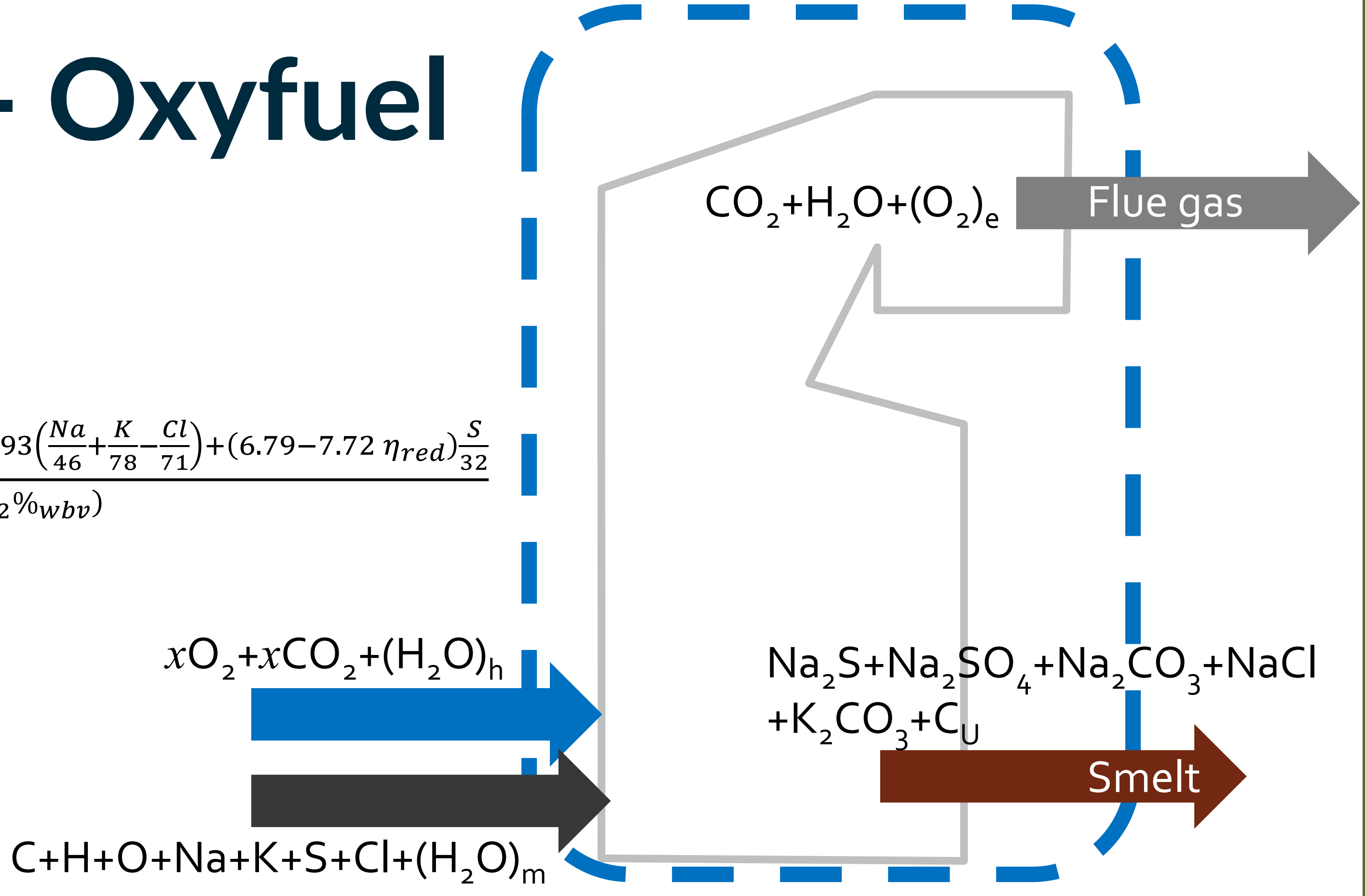
- Aligned with TAPPI recovery boiler performance calculation (TIP 0416-01)
- Thermodynamic data from NASA polynomials (NASA/TP—2002-211556)
- Steam properties from Moran & Shapiro (2006)



Methodology - Oxyfuel

- Modification of TAPPI calculation
  - flue gas moles:

TAPPI calculation: $$(FG)_w = \frac{\frac{4.86}{12}C+\frac{2.93}{2}H+\left(\frac{H_2O(m+h)}{18}\right)-\frac{3.88}{32}O+0.93\left(\frac{Na}{46}+\frac{K}{78}-\frac{Cl}{71}\right)+(6.79-7.72\,\eta_{red})\frac{S}{32}}{(1-4.8\,O_2\%_{wbv})}$$



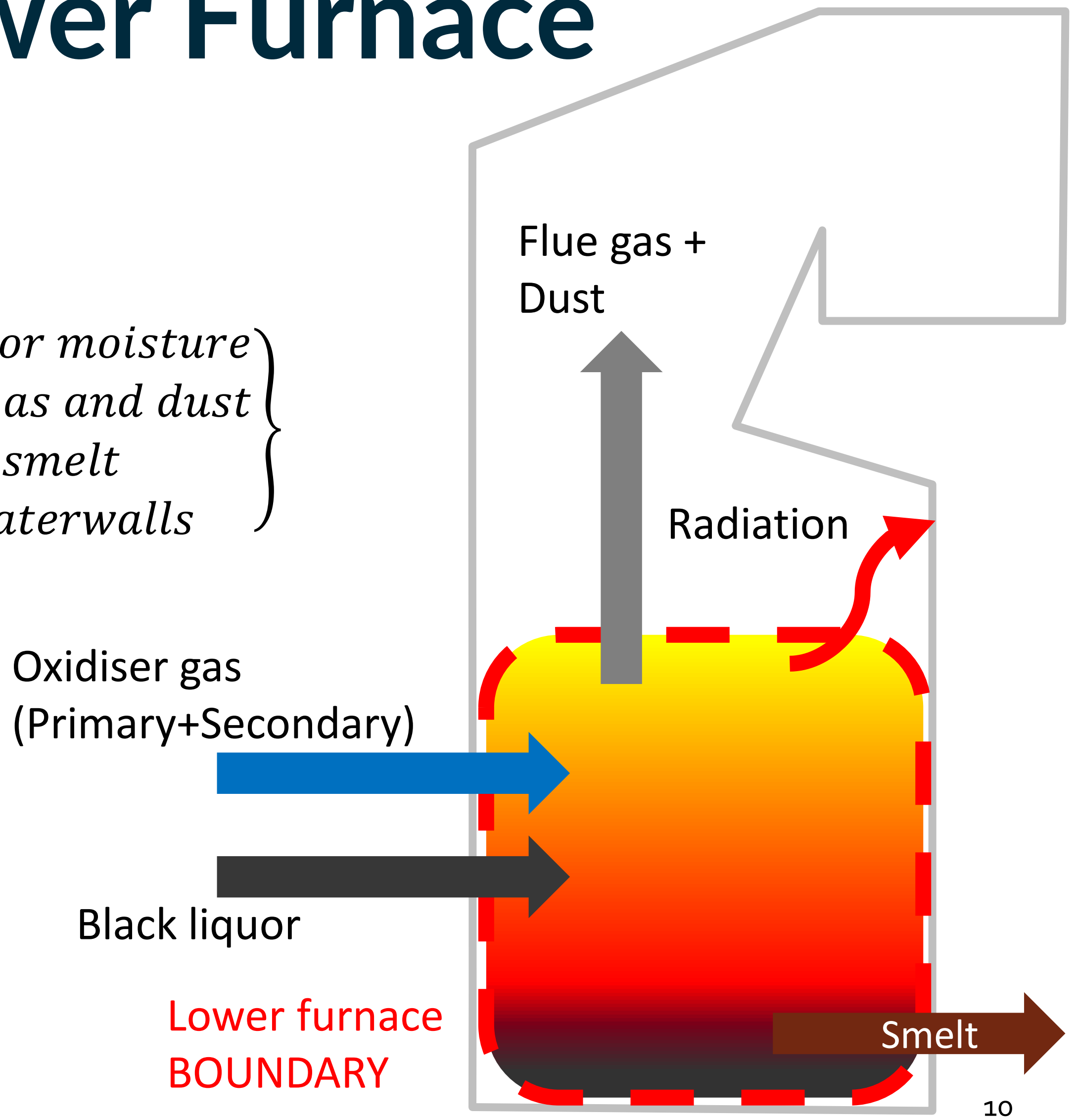
  - Mass balance derives new calculation for flue gas moles:

$$(FG)_w = \frac{\left(1+\frac{x_{CO_2}}{x_{O_2}}\right)\frac{C-C_u}{12}+\left(1+\frac{x_{CO_2}}{2\,x_{O_2}}\right)\frac{H}{2}+\left(\frac{H_2O_{(m+h)}}{18}\right)-\frac{x_{CO_2}}{x_{O_2}}*\frac{O}{32}+\left(\frac{x_{CO_2}}{2\,x_{O_2}}-1\right)\left(\frac{Na}{46}+\frac{K}{78}-\frac{Cl}{71}\right)+\left(1+\frac{x_{CO_2}}{x_{O_2}}\left(\frac{3}{2}-2\eta_{red}\right)\right)\frac{S}{32}}{\left(1-\left(\frac{x_{CO_2}}{x_{O_2}}+1\right)*O_2\%_{wbv}\right)}$$

Methodology – Lower Furnace

- Lower furnace energy balance (Adams, 1997)

$$\left\{\begin{array}{c} Chemical\ energy\ from \\ black\ liquor\ combustion \\ +\ Sensible\ energy\ of \\ black\ liquor\ and\ oxidizer \end{array}\right\} = \left\{\begin{array}{c} Latent\ heat\ of\ black\ liquor\ moisture \\ +\ Sensible\ heat\ of\ flue\ gas\ and\ dust \\ +\ Sensible\ heat\ of\ smelt \\ +\ Radiation\ heat\ to\ waterwalls \end{array}\right\}$$



Methodology – Lower Furnace

- Chemical energy from partial combustion $= \dot{m}_{DS}(LHV)F_h$
- Sensible energy of black liquor and oxidizer
$$= (\dot{m}_{DS} + \dot{m}_w + \dot{m}_{SC})C_{P,liq}\left(T_{liq,i} - T_{ref}\right) + \dot{m}_{ox}C_{P,ox}\left(T_{ox,i} - T_{ref}\right)$$
- Latent heat of black liquor moisture $= \dot{m}_w \Delta h_v$
- Sensible heat of flue gas and dust $= (\dot{m}_{FG} + \dot{m}_{dust})C_{P,FG}\left(T_F - T_{ref}\right)$
- Sensible heat of smelt $= \dot{m}_{smelt}C_{P,smelt}\left(T_{smelt} - T_{ref}\right)$
- Radiation to waterwalls $= \left(\varepsilon_g 4WL_F + \left\{1 - 0.6\ \varepsilon_g\right\}W^2\right)\sigma^{\circ}\left(T_F - T_{ref}\right)$

Air Reference Case - Inputs

- BLDS Heating value (HHV=13.2 MJ/kg)
- BLDS concentration (81.3 wt%DS)
- Excess O_2 in flue gas (3.0 v%)
- Furnace Prim+Secd air (65%)
- BL flow (~5300 tDS/d)
  - Floor loading (3.61 MW/m^2)
- HBL inlet temperature (140°C)
- Smelt temperature (950°C)
- Air inlet temperature (150°C)
- Flue gas exit temperature (180°C)
- Process steam conditions (515°C, 110 bar)

- BLDS composition (%w):

Carbon	32.20%
Hydrogen	3.30%
Oxygen	33.91%
Sodium	21.40%
Potassium	2.40%
Sulfur	6.40%
Chloride	0.30%
Nitrogen	0.09%

Reference Boiler

- Steam: 2.782 kg/kgDS
- Flue gas: 5.119 kg/kgDS

  183.3 mol/kgDS

  Composition:

  12.55%v CO_2

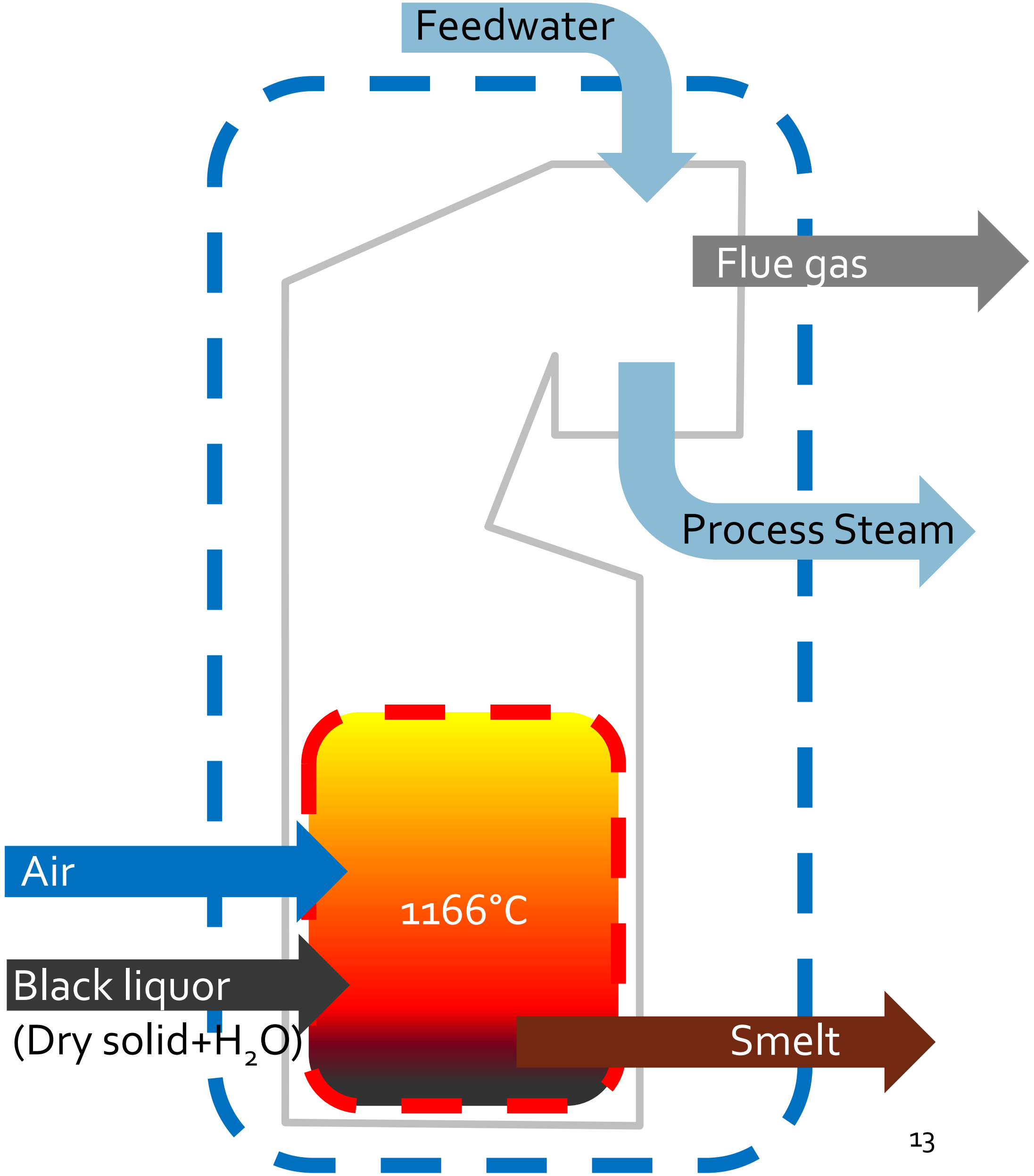
  62.28%v N_2

  0.020%v CO

  0.007%v SO_2

  3.00%v O_2

  22.14%v H_2O



Oxyfuel Boiler

- Steam: 2.782 kg/kgDS
- Flue gas: 5.000 kg/kgDS

  138.9 mol/kgDS

  Composition:

  67.76%v CO_2

  0.023%v N_2

  0.026%v CO

  0.010%v SO_2

  2.98%v O_2

  29.20%v H_2O

- O_2 from ASU:

  0.828 kg/kgDS

- To CCS (dry):

  1.045 kg/kgDS

  Composition:

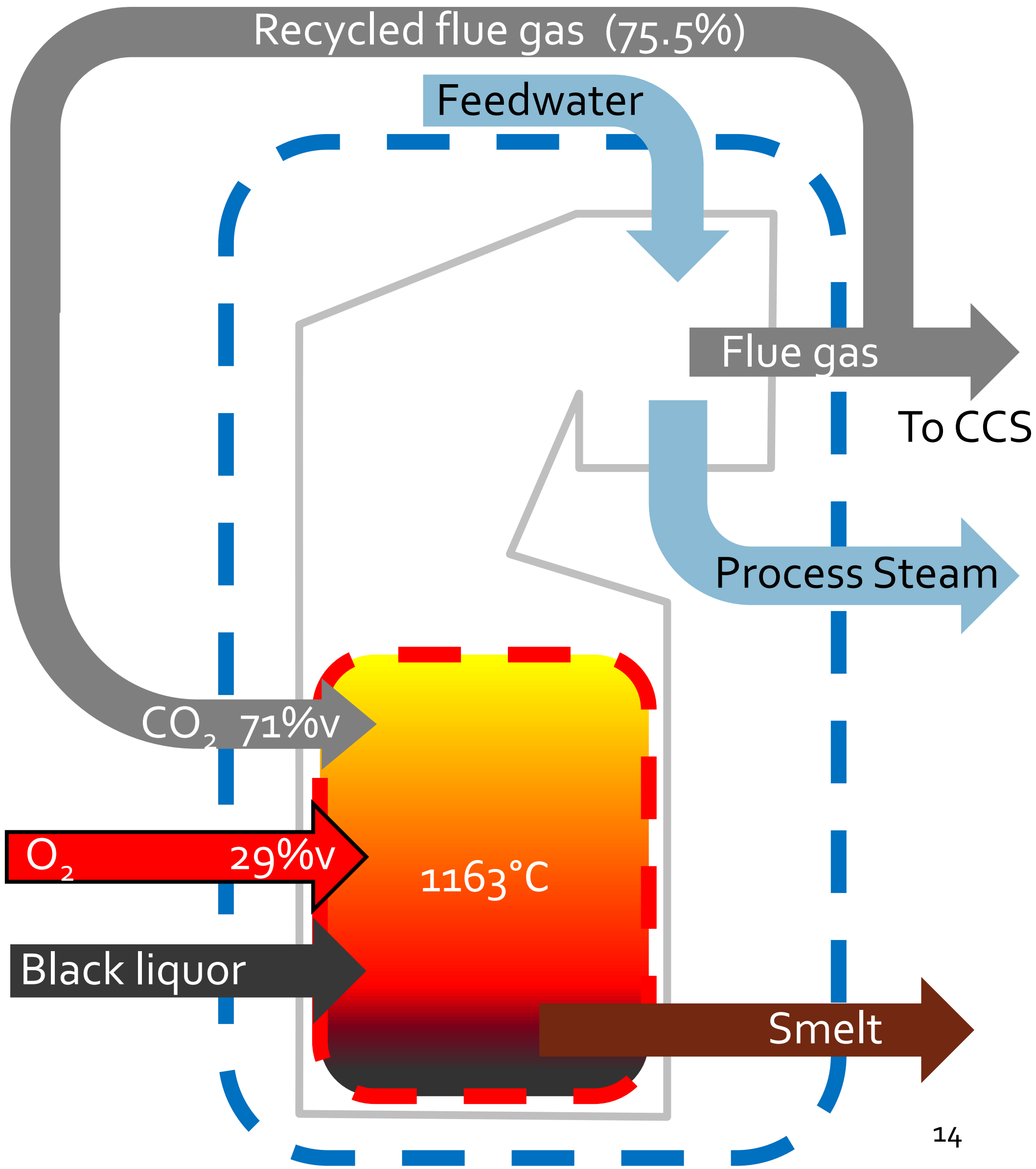
  95.71%v CO_2

  0.033%v N_2

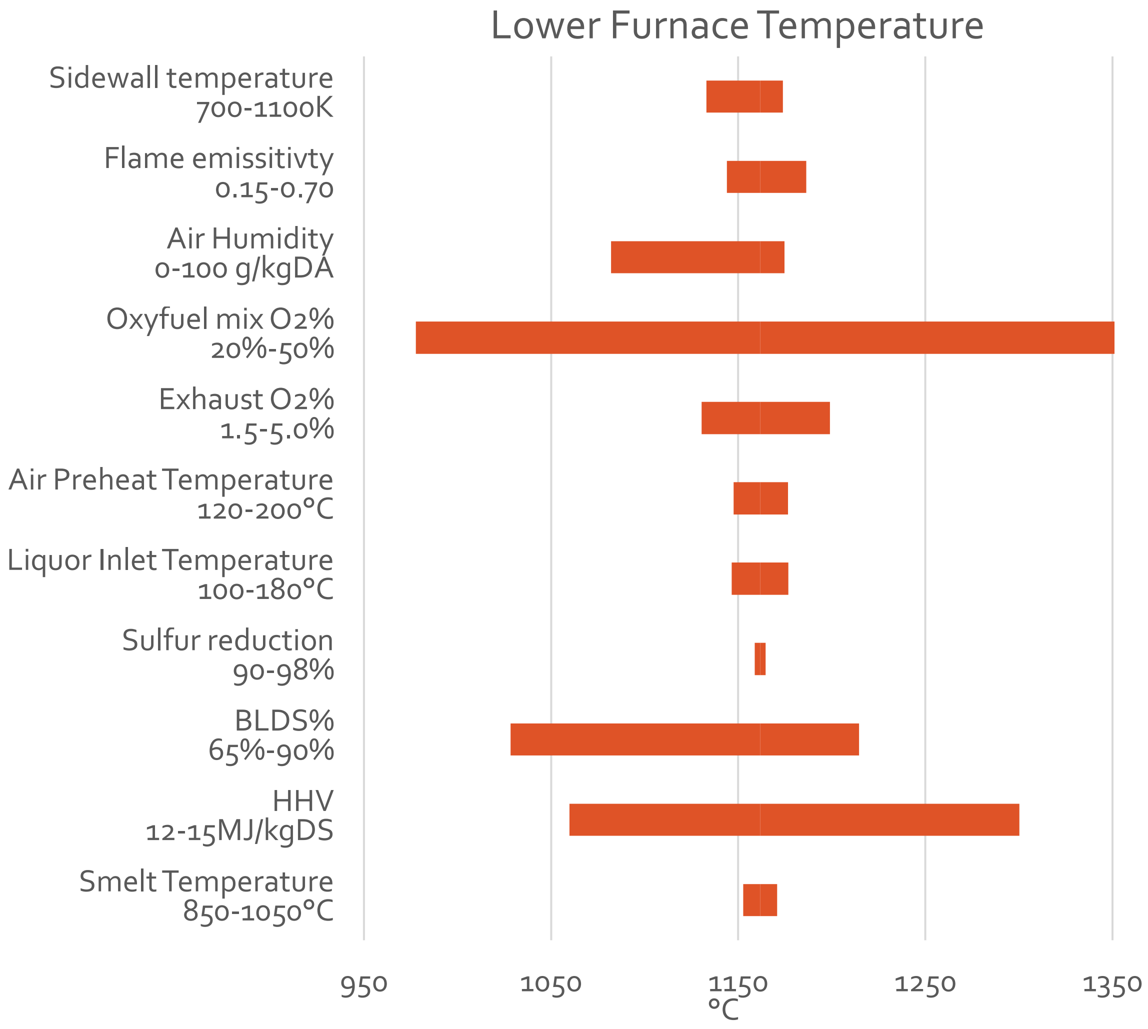
  0.037%v CO

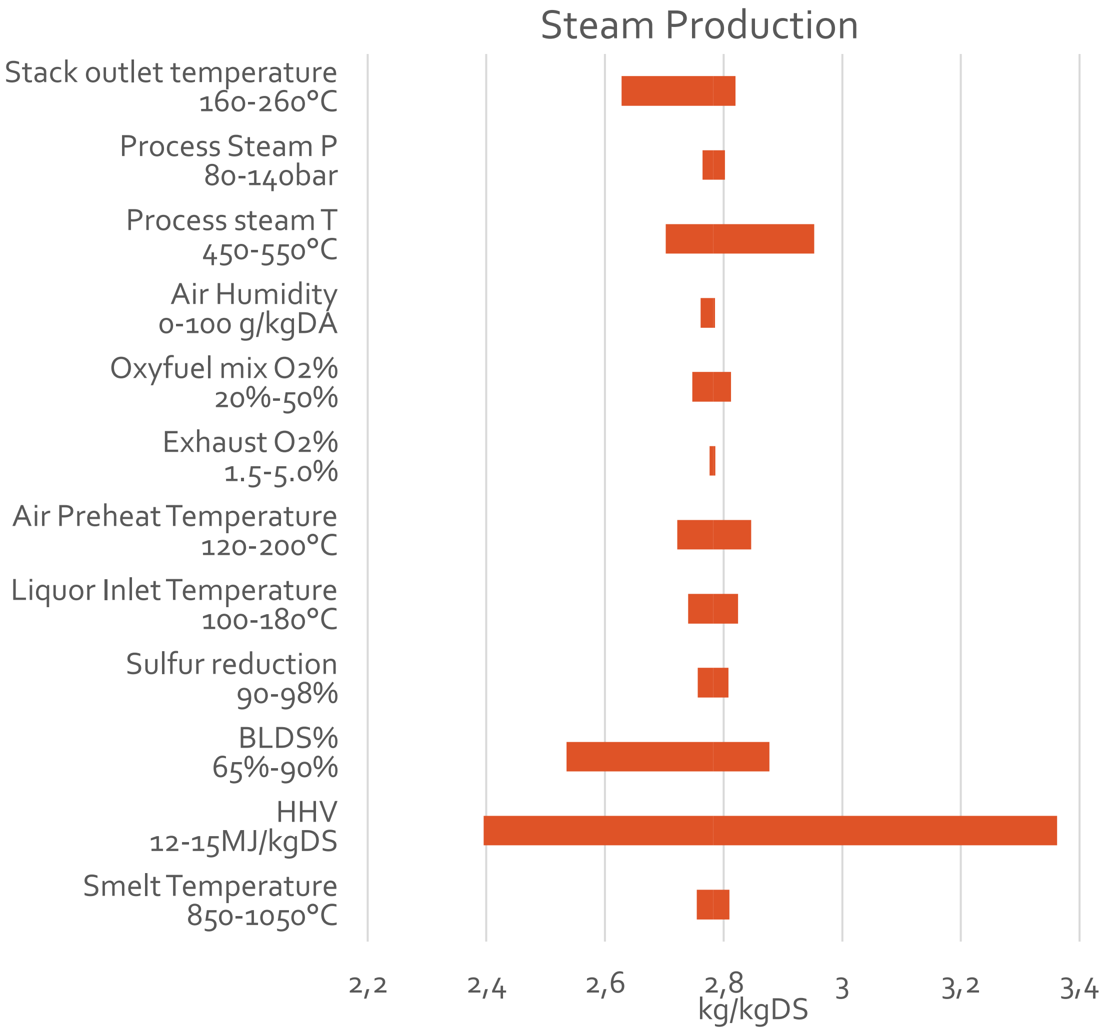
  0.014%v SO_2

  4.21%v O_2

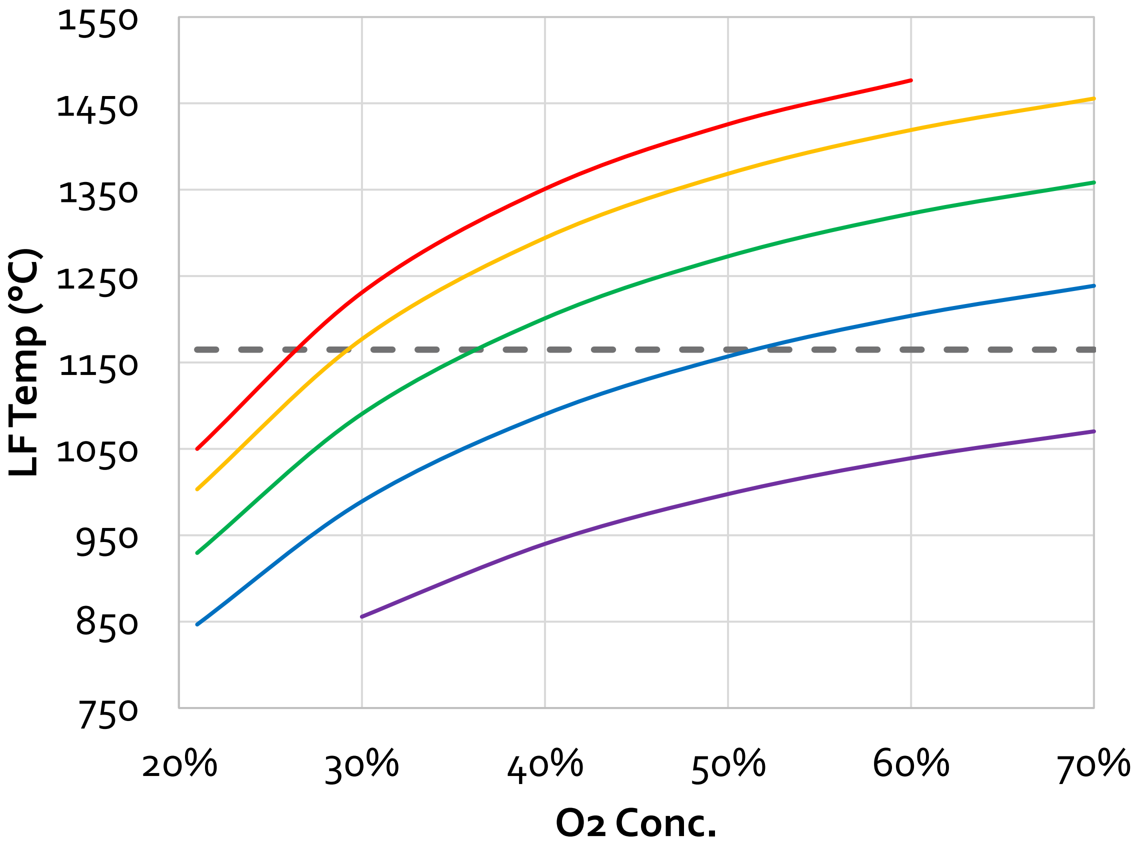


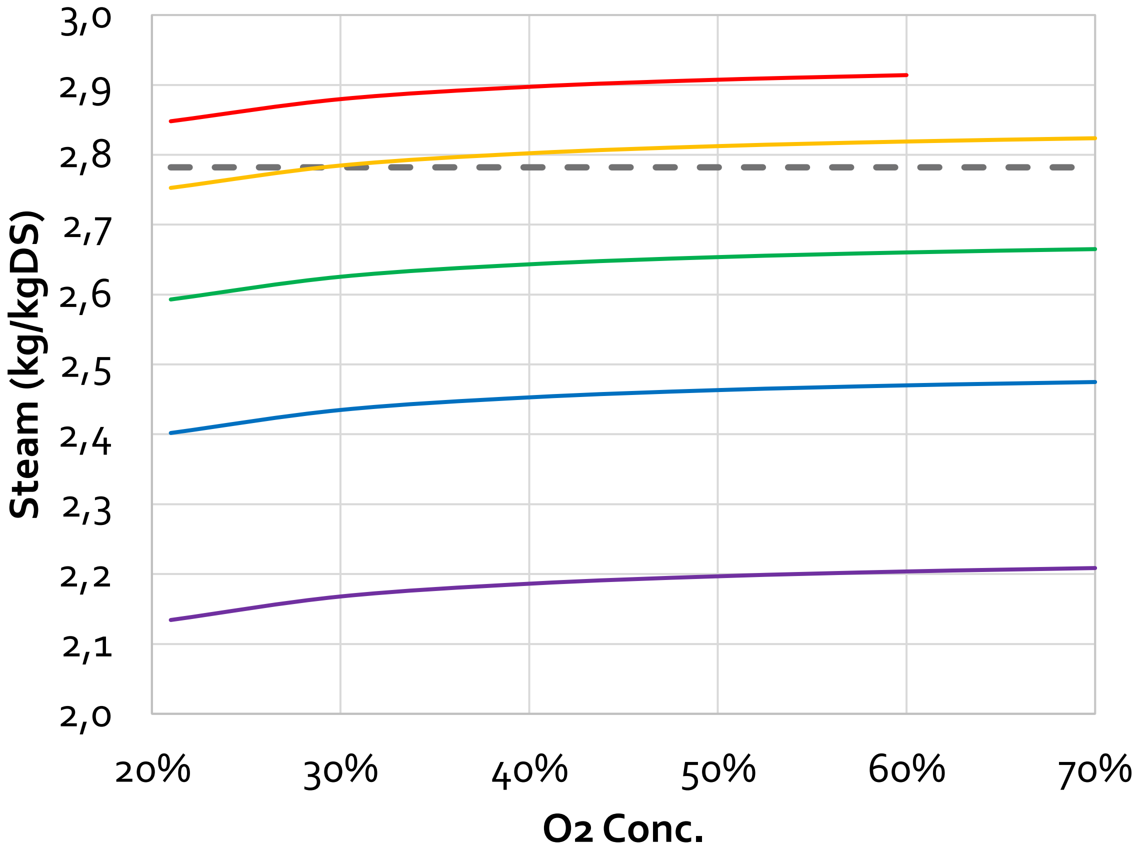
Oxyfuel Sensitivities





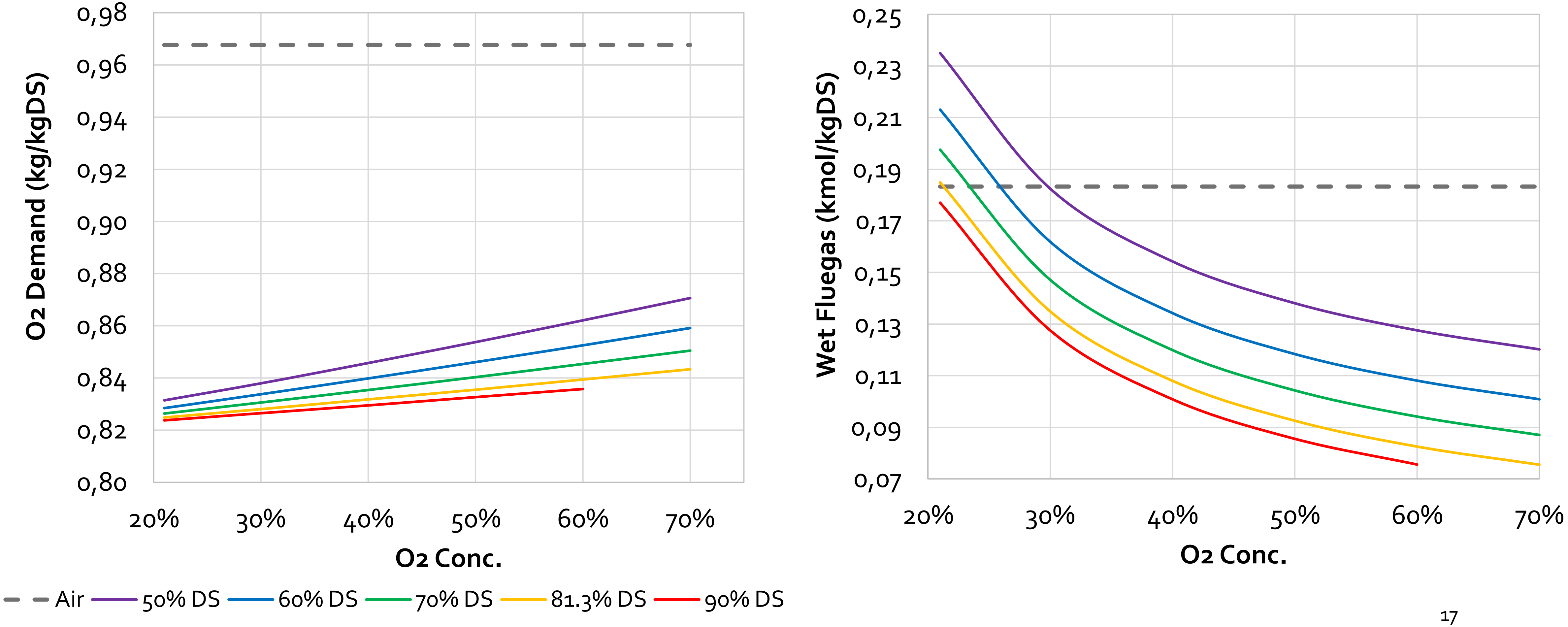
Oxyfuel Variations





Air
50% DS
60% DS
70% DS
81.3% DS
90% DS

Oxyfuel Variations



Oxyfuel gas flows

- **Alternate case**: equivalent molar flows in boiler
  - Increase BLDS inputs: 6760 tpd (+27%)
  - Floor loading: 4.59 MW/m^2
- Steam: 2.779 kg/kgDS (+46.13 kg/s)
- Flue gas: 5.238 kg/kgDS (+94.6 kg/s)

  144.2 mol/kgDS

  Composition:

  68.75%v CO_2

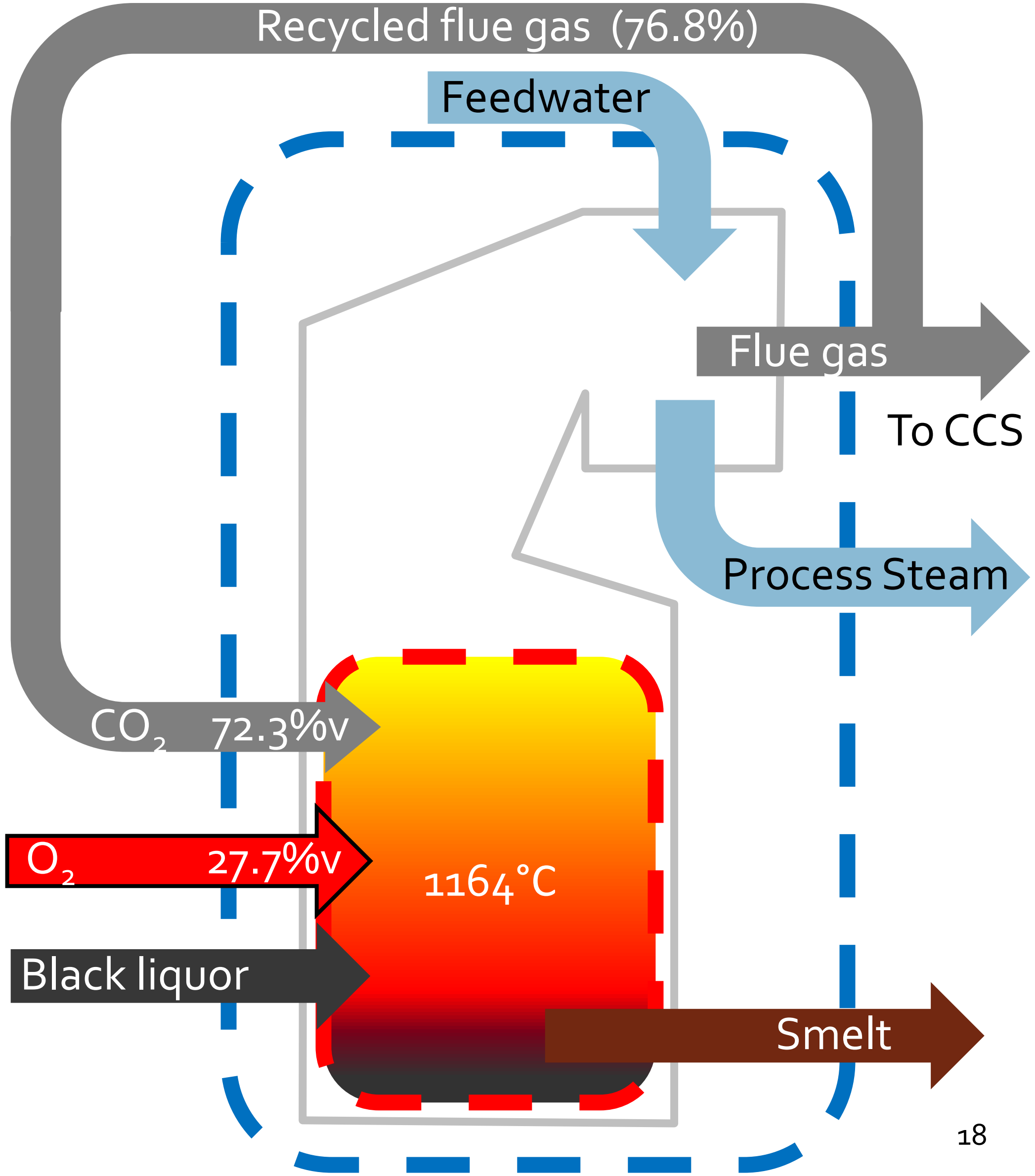
  0.022%v N_2

  0.025%v CO

  0.009%v SO_2

  3.00%v O_2

  28.20%v H_2O

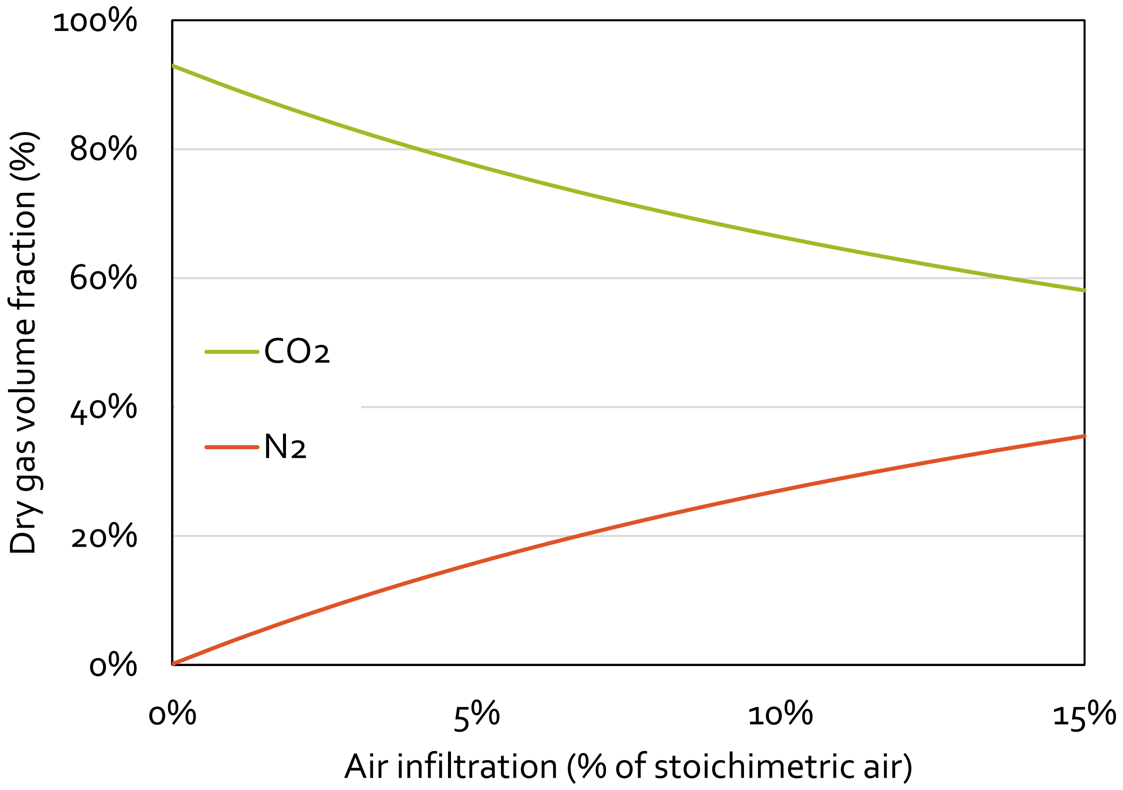


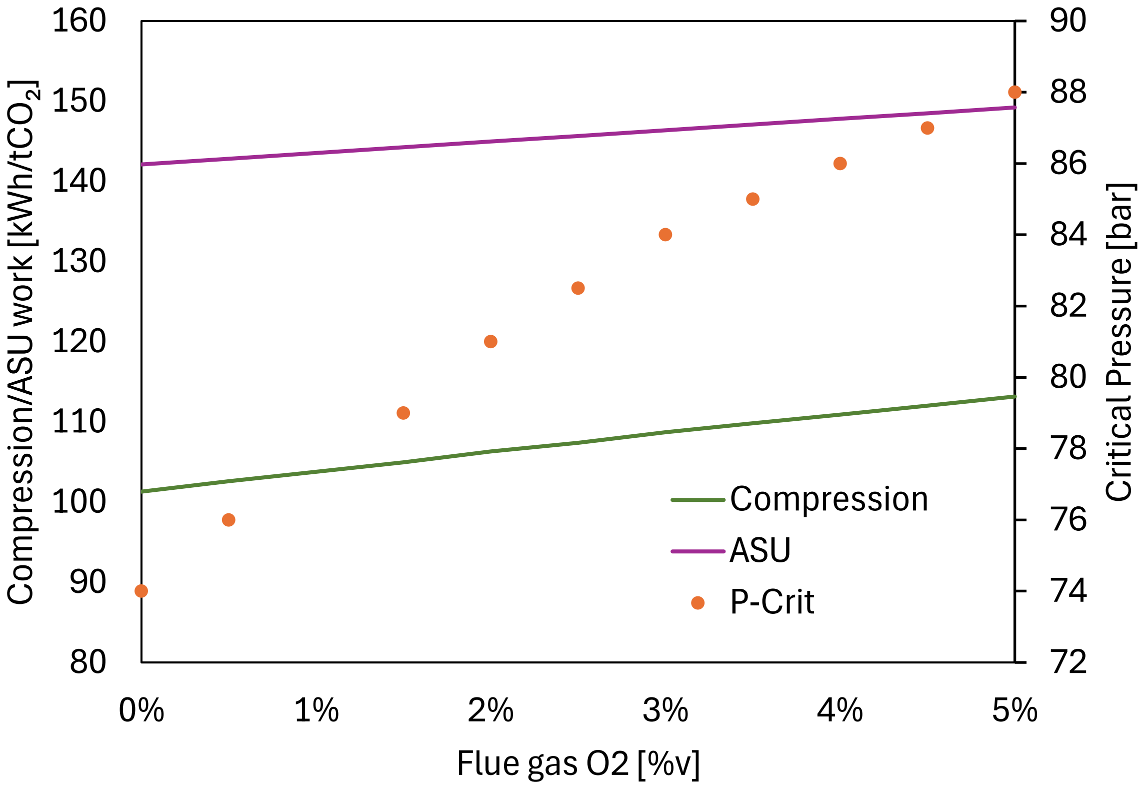
CO_2 quality

Gas quality requirements for selected CCS storage projects

	DYNAMIS (deVisser, 2008)	Porthos (2022)	Northern Lights (2024)	NETL (2019)	Oxy-Kraft Boiler
CO_2	>95.5%	>95%	>99.81%	>95%	**95.705%**
H_2O	500 ppm	<70 ppm	<30 ppm	500 ppm	**-**
O_2	-	<40 ppm	<10 ppm	< 1000 ppm	**4.212 %**
CH_4	<4%	<1%	<100 ppm	<4%	**-**
CO	2000 ppm	<750 ppm	<100 ppm	<35 ppm	**370 ppm**
N_2	<4%	<2.4%	<50 ppm	<4%	**330 ppm**
Ar	<4%	<0.4%	<100 ppm	<4%	**-**
H_2	<4%	<0.75%	<50 ppm	<4%	**-**
H_2S	200 ppm	<5 ppm	<9 ppm	<0.01%	**-**
SO_2	-	<20 ppm	<10 ppm	<100 ppm	**140 ppm**

Air infiltration and excess O_2





Conclusions

- Lower furnace Oxyfuel conditions (temperature) are influenced by dry flue gas recycling and BL dry solids concentration
  - Control of these parameters can be used to set lower furnace temperature
  - Higer amounts of FGR and BL water content reduce specific steam production in the boiler
- Oxyfuel conditions reduce volume flows through the boiler
  - Increase firing rate/floor loading possible to match volume flows
- Flue gas quality may be unsuitable for direct sequestration – additional purification required
  - Minimizing contaminants, infiltration air, and excess O_2 reduces energy requirements of purification
- Effect of Oxyfuel conditions on black liquor combustion and smelt recovery is uncertain
  - Parallel research on this topic ongoing within the Oxy-Kraft project

Acknowledgements

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    - International Paper Inc., USA
    - Valmet Technologies Oy, Finland
    - Valmet Ab, Sweden