Flexible chemical looping combustion pathways for sustainable bioenergy conversion

Webinar on chemical-looping

Jan.26th, 2026

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Carbon capture, 1998

GREENHOUSE GAS CONTROL TECHNOLOGIES

Proceedings of the 4th International Conference
on Greenhouse Gas Control Technologies,
30 August - 2 September 1998, Interlaken, Switzerland

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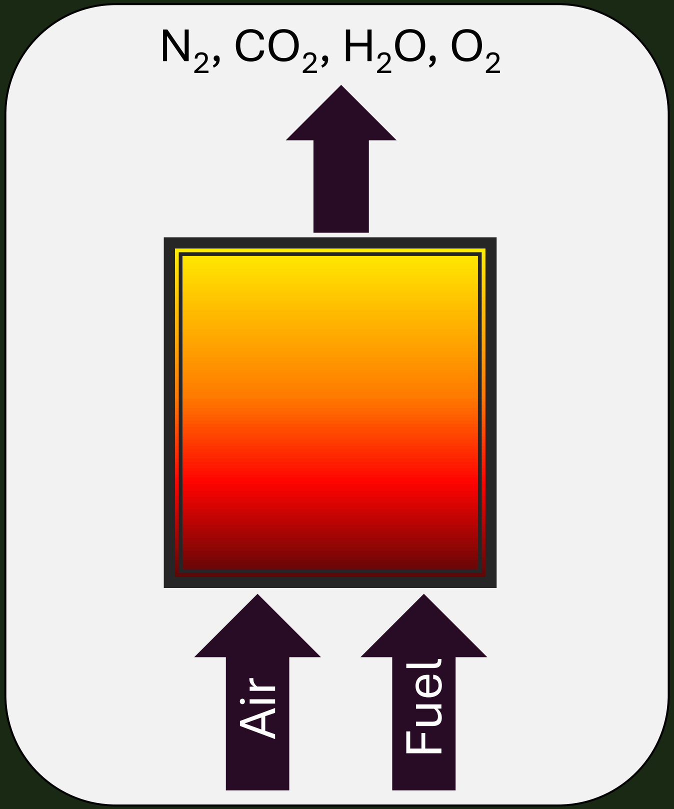
A problem with mixtures

”Normal” combustion
4-15 vol% CO_2, water, nitrogen, some oxygen, impurities, ash

To begin, we need
>95 vol% CO_2

Range of gaseous streams available:
0.04 – 99% CO_2



Normal combustion

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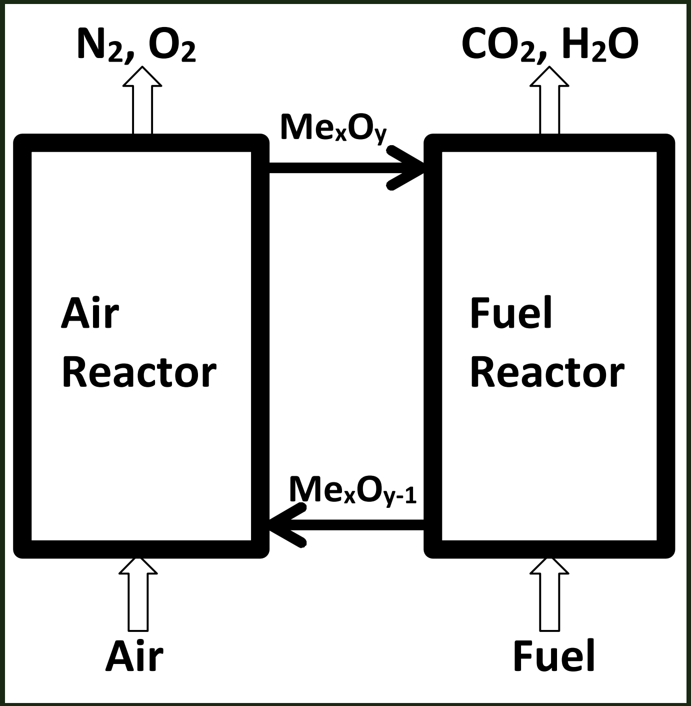
Carbon capture and chemical-looping



Air Reactor:

$$(n+\tfrac{1}{2}m)O_2 + (2n+m)Me_xO_{y-1} \leftrightarrow (2n+m)Me_xO_y$$

Fuel Reactor:

$$C_nH_{2m} + (2n+m)Me_xO_y \leftrightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1}$$

Net Reaction:

$$C_nH_{2m} + (n+\tfrac{1}{2}m)O_2 \leftrightarrow nCO_2 + mH_2O$$

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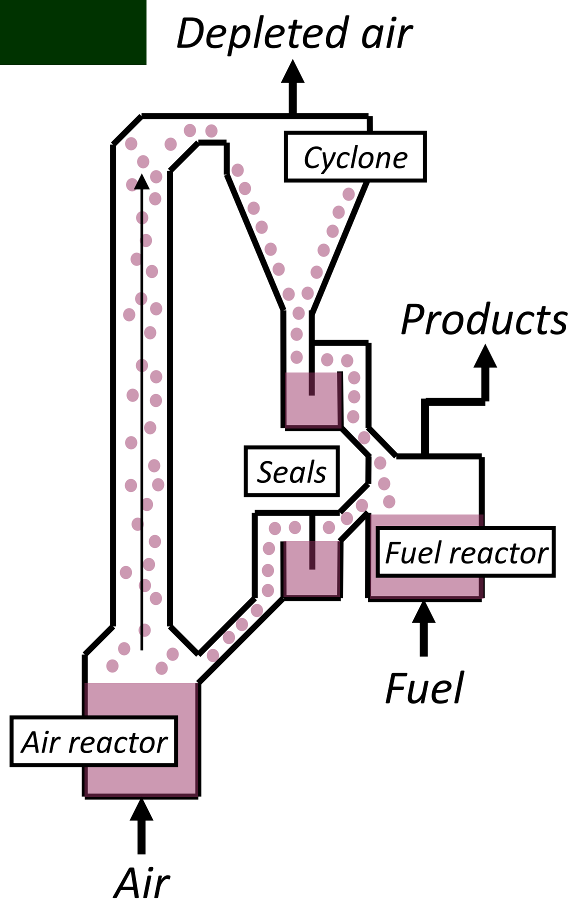
Basic reactor design

- Sand-like particles of oxygen-carrier material (0.1-0.4 mm) as bed material.
- High gas velocity (2-5 m/s) in the air reactor which acts as riser, particles are blown upwards and into a cyclone.
- The particles are transported by gravity to the fuel reactor in which they are reduced by fuel, then continues to the air reactor.
- Gas leakage between the reactors is prevented by fluidized particle seals.
- Typically, near atmospheric pressure and temperature 800-1050°C.
- Many variations have been proposed and tested. Still, the basic setup serves its purpose well.



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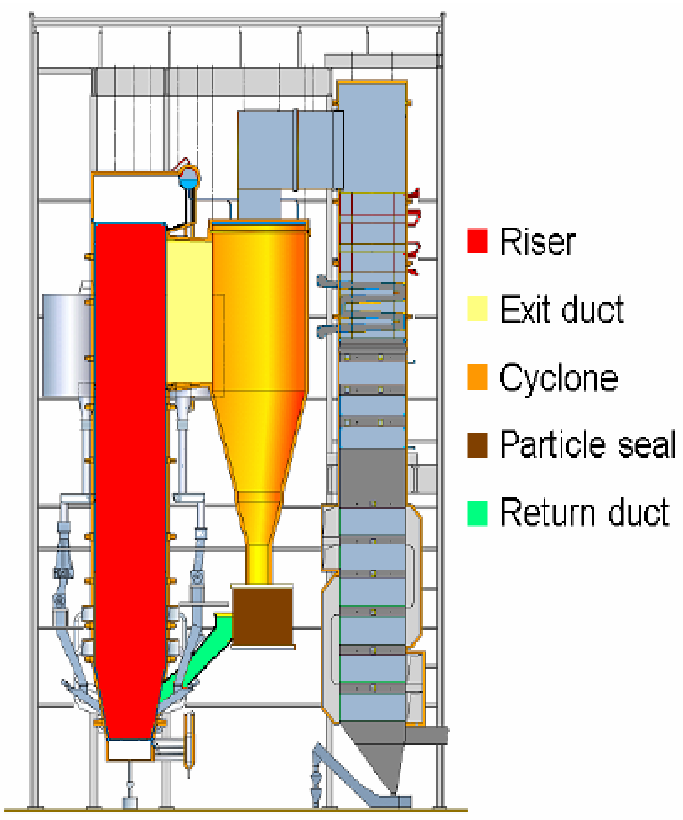
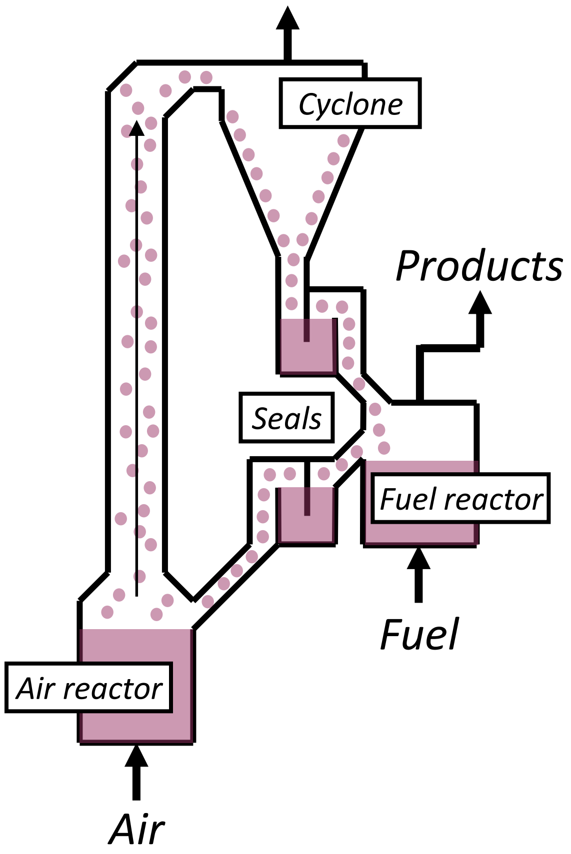
Circulating Fluidized Bed boiler (CFB)





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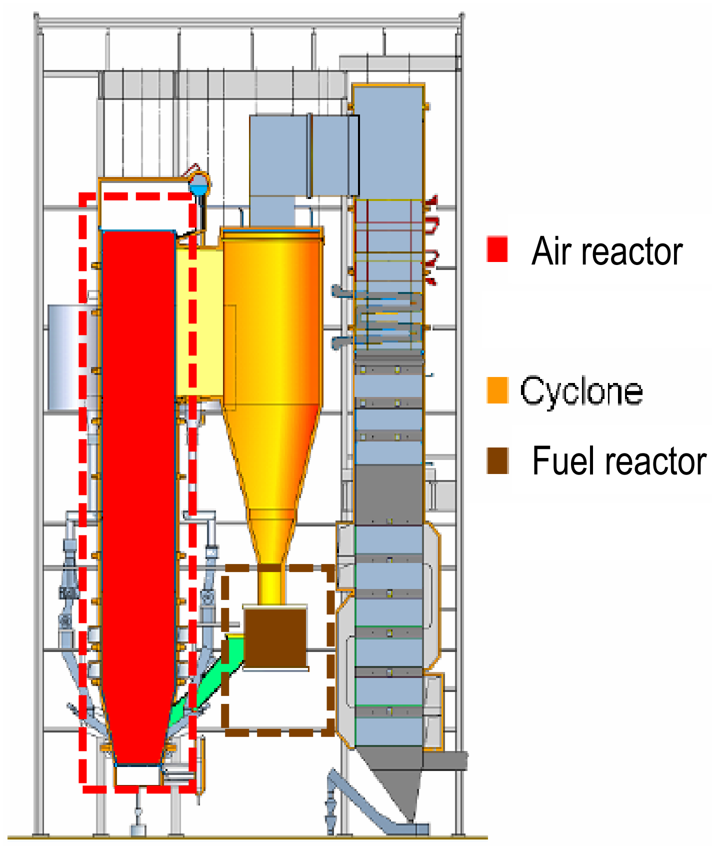
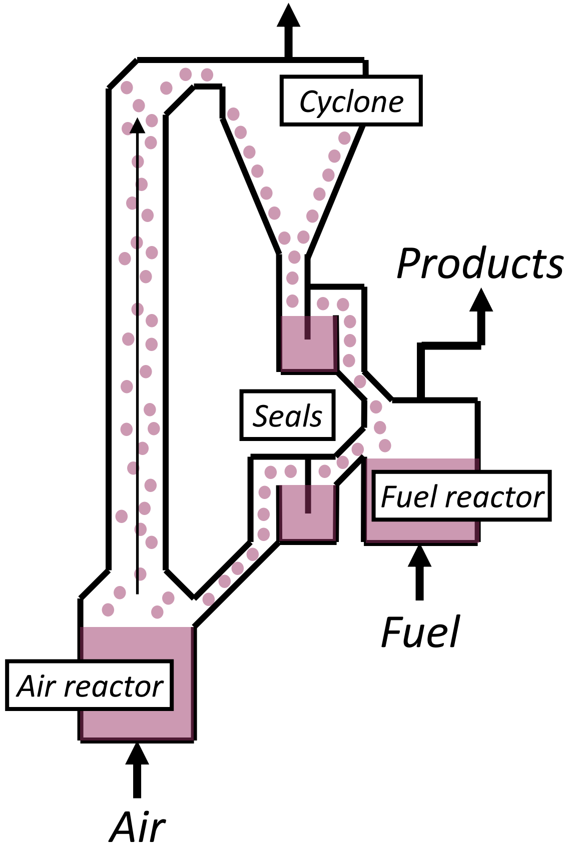
Circulating Fluidized Bed boiler (CFB)





Why even bother with CLC?

- CLC can reduce the energy penalty for CO_2 capture. In theory, there is no energy penalty compared to conventional combustion.
- CLC can have close to 100% capture rate without extra costs or efforts.
- CLC does not require harmful chemicals. The oxygen carrier can be mineral ores
- As fuel conversion occurs only in FR, the AR is should have no or low fractions of reactive ash species=lower high-temperature corrosion, perhaps enabling higher steam data.
- Similarities with CFB provides some interesting opportunities with respect to operation in different "modes"

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Chemical-looping at Chalmers

Overall goals

- *Develop technologies for negative emissions, focus on chemical-looping processes*
- *Develop adjacent technologies with oxygen carriers*

Research questions

- *How do different impurities behave in the special environment? Can we improve the mass transport in the fluidized bed? Are there unexplored phases which could be used as oxygen carriers ? Can we produce hydrogen efficiently? How can we best support development for rapid deployment?*

Tools to answer research questions

- *Different sizes of research from XS to L*

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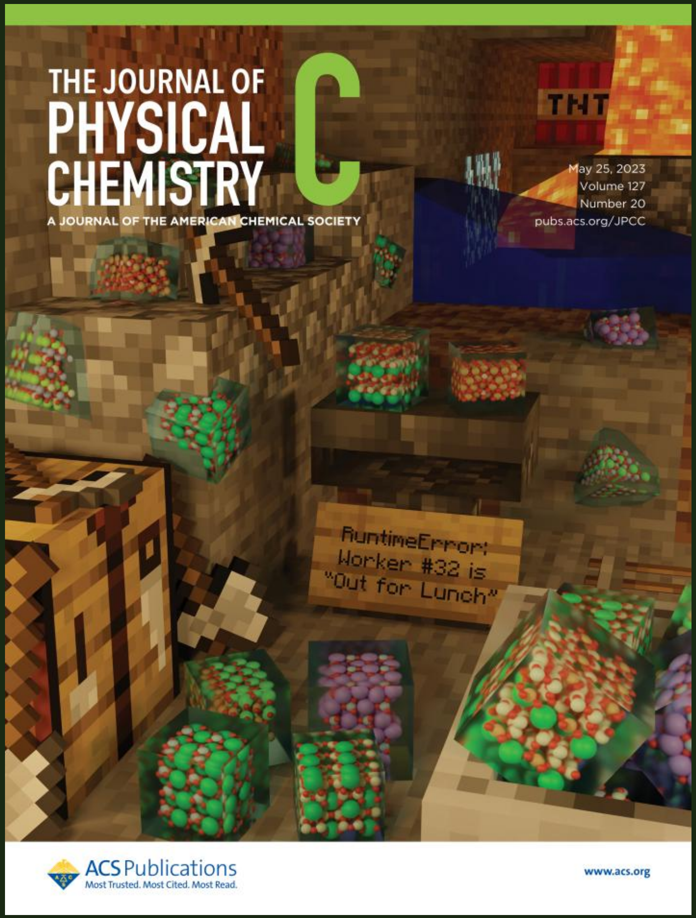
Extra Small (XS)

Main goals

Establish methodologies for discovering and evaluating new oxygen carriers using a combination first-principles calculations, machine learning and data mining

Method/tools

- Density functional theory
- Machine learning
- Big data



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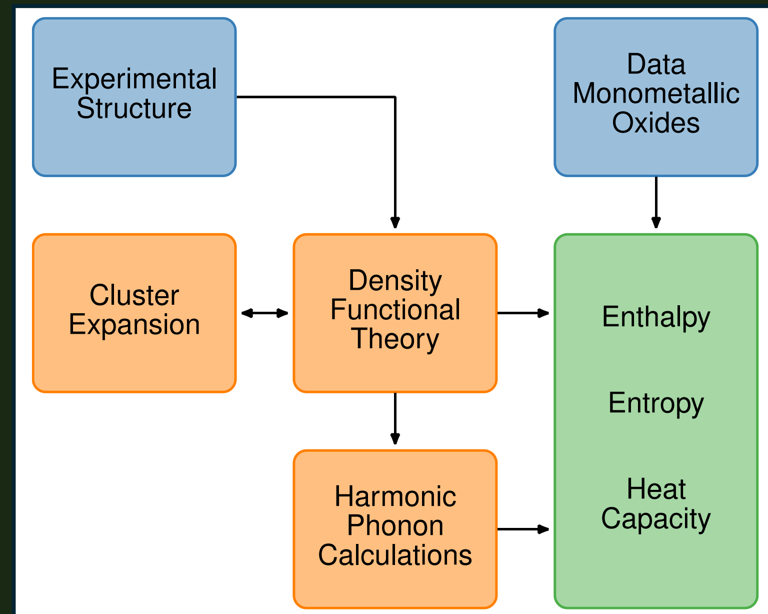
Thermodynamics by DFT

Main goals

Estimate the properties of materials missing from thermodynamic databases

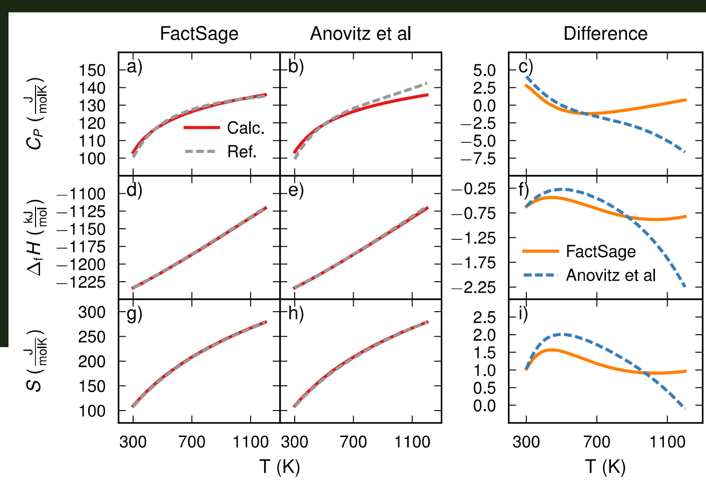
Tools

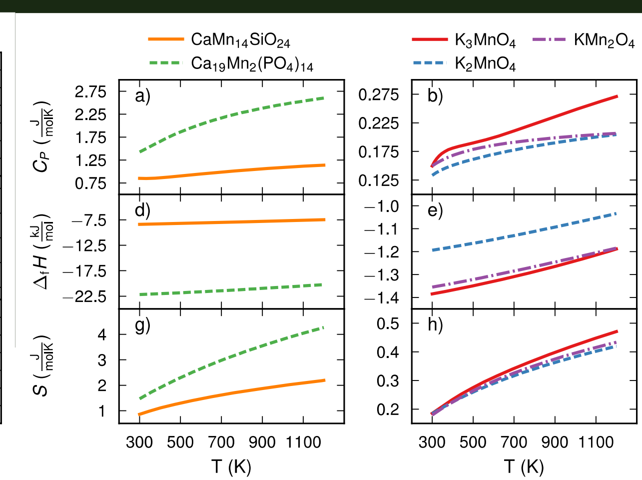
- Density functional theory
- Cluster expansions
- Harmonic phonon calculations



Main result

- Exceptional agreement for $FeTiO_3$
- Improved predictions for K-Fe-Ti-O and K-Mn-O systems





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Prediction of phases

Main goals

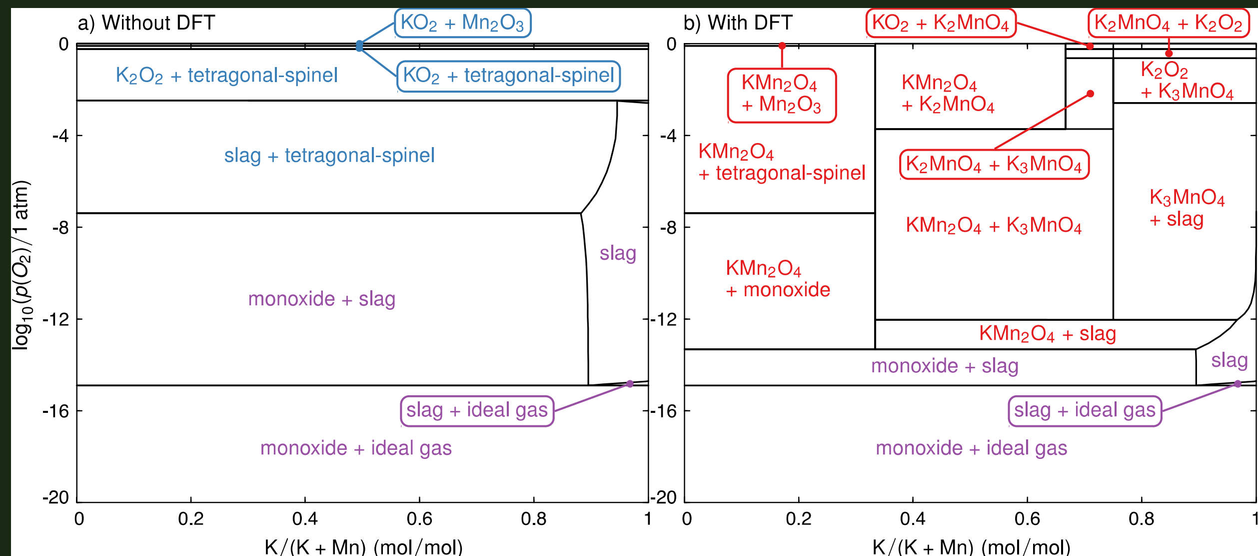
Perform thermodynamic calculations with FactSage® based on properties obtained from first principles calculations

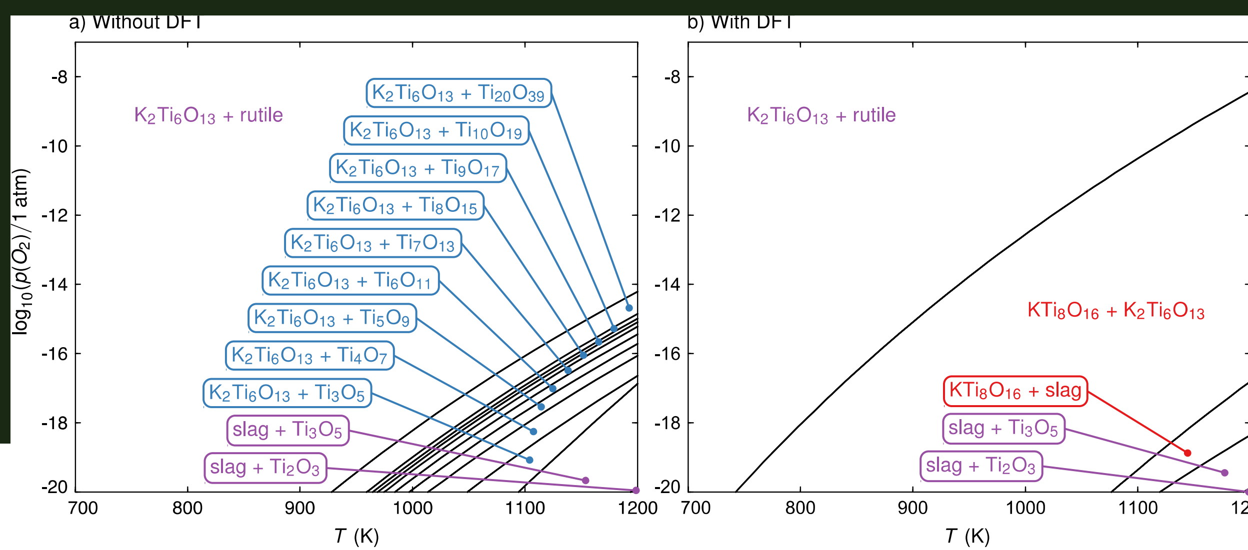
Tools

- First principles data
- FactSage ®
- Commercial databases

Main result

- New phases appear
- Profound differences are observed for K-Mn-O and K-Ti-O





Small (S)

Main goals

- Oxygen carriers in chemical looping
  - Ash interaction with oxygen carriers
    - Mechanisms of sulfur interaction with ilmenite
  - Fate of important impurities, trace elements

Method/tools

- XRD (CMAL, Physics)
- SEM/EDX (CMAL, Physics and Chemistry and Chemical Engineering)
- BET (Applied Chemistry)
- XPS (Industrial and Materials Science)
- Thermodynamic calculations

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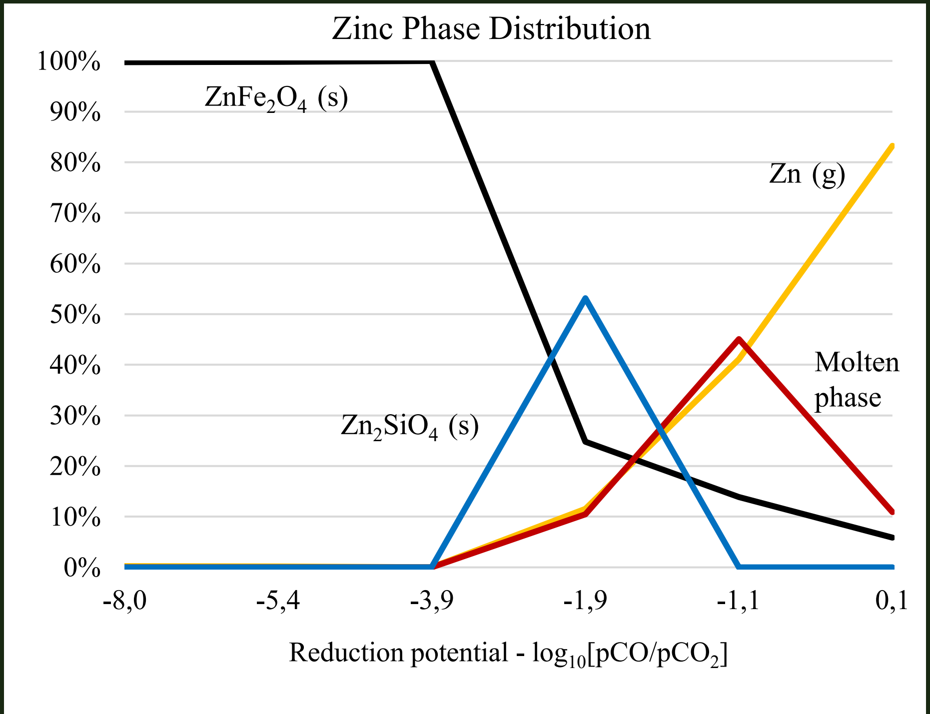
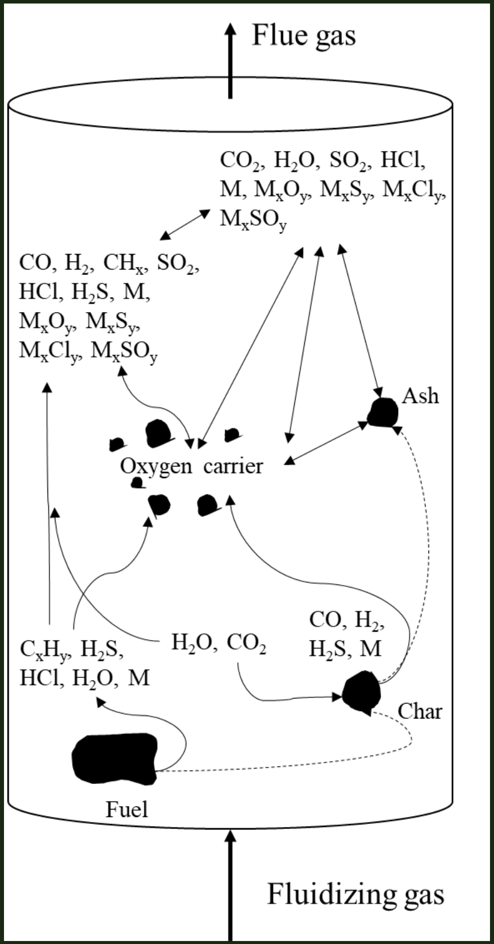
Small (S)

Main results

- Zinc and copper bind to ilmenite as ferrites while lead may form titanates
- Volatilization of trace elements increases with reducing atmospheres





Possible trace element (M) pathways in a fluidized bed. *Stanicic, I.*

Zinc phase distribution during waste combustion showing increased volatility at higher reduction potentials. Calculation performed in FactSage. *Stanicic, I.*

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Medium (M)

Main goals

- Reactivity with different fuels
- Heat and mass transfer

Method/tools

- Batch fluidized beds
- Signal analysis
- TGA

Large (L)

Main goals

- Evaluation of CLC and CLG at realistic conditions
- Investigating alkali release and tar formation in CLC/CLG of biomass
- Improving gas-solid interactions using cold flow model

Method/tools

- Pilot units up to 100 kW
- Cold flow models
- Gas analysis, alkali and tar measurements, attrition measurements

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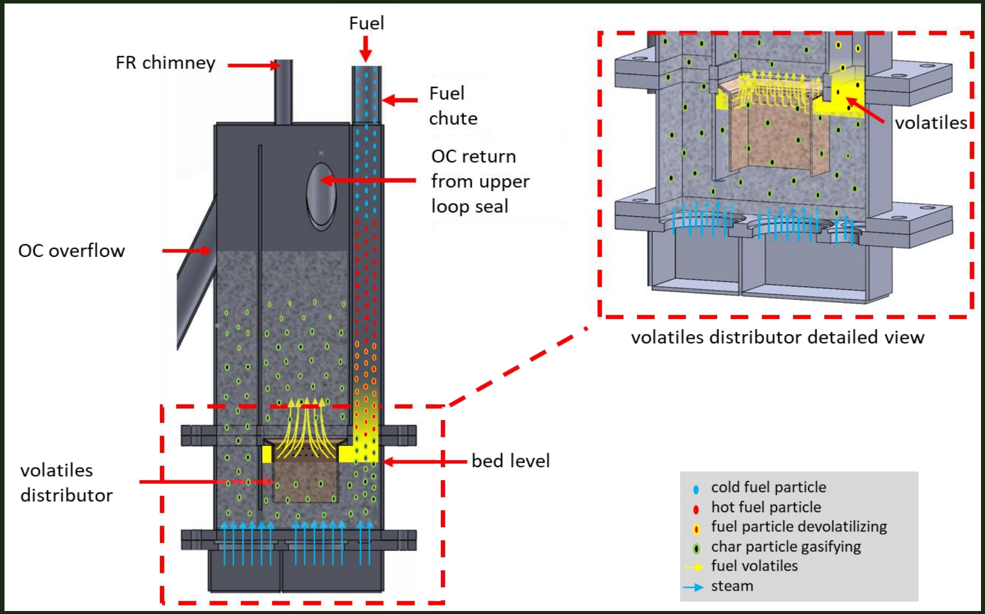
10 kW CLC/CLG unit for solid fuels

- Commissioned the new 10 kW pilot for CLC and CLG of high volatiles solid fuels
  - ✓ Up to 10% gas conversion improvement due to volatiles distributor
  - ✓ Newly implemented solid and tar sampling systems

- Commissioned the modular SID system for ash chemistry studies



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Confined Fluidized Beds

- In confined fluidization also known as packed-fluidized bed, inert stagnant packings of much larger size than the fluidized particles are applied to break down the larger bubbles.
- Packed-fluidized beds could be of high interest for CLC.
- Application of packings can improve gas-solid mass transfer as well as fuel conversion. Thus, facilitating complete combustion of fuel gases, volatiles, and char particles originating from the reactions in FR.

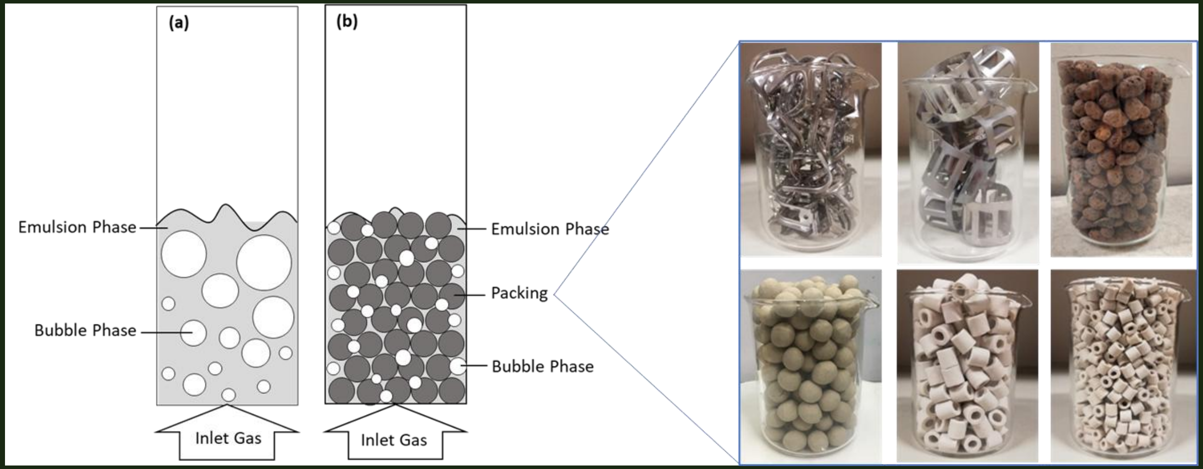

Figure. Illustration of a) conventional BFB, b) packed-fluidized bed.

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Extra Large (XL)

?

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A breakthrough for CLC?

- Operation of 5 MW autothermal CLC demo in China.
- Air reactor is 40 m high, with 10 m/s fluidization velocity.
- Temperature was 1000C in AR and 950C in FR
- Fuel was coal and petroleum coke
- Oxygen carrier: Ilmenite

- ➢ Operation was continued autothermally for almost 70 h
- ➢ Very high gas conversion with an oxygen demand of less than 2.5%.

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Oxygen Carrier Aided Combustion (OCAC)

- OCAC involves the use of oxygen carriers in conventional fluidized-bed boilers.
- Since 2014 OCAC has been evaluated in >15 commercial boilers.
- Main benefit is reduced need for excess air and increased load of 5-15%.
- Main drawback is high cost and complications related to ash disposal.
- Current focus is switch from virgin bed material towards industrial byproducts.
- Main partner is Eon, with materials provided by Titania, Boliden, SSAB, Sibelco etc.
- Positive for CLC since we learn a lot about e.g. material logistics, waste disposal etc.

Chalmers lab

2013

Chalmers 10 MW CFB

Feb 2014

Eon Händelöverket 75 MW CFB

Apr 2014

Now evaluated in >15 commercial facilities (20-300 MW) with wood chips, waste wood fuel and municipal solid waste, using ilmenite, manganese ore, steel converter slag and copper smelter slag as bed material

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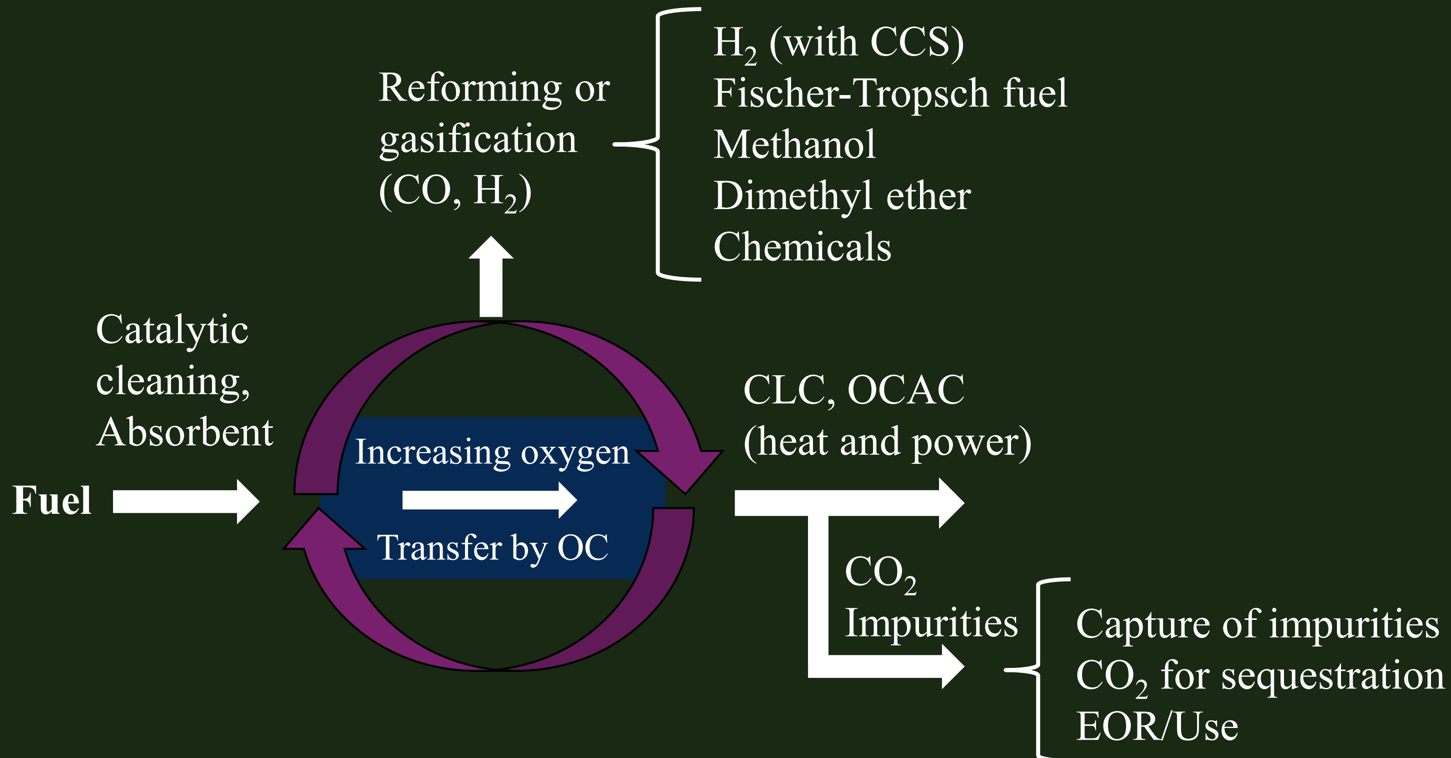
Oxygen transfer



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Bio-Flex CLC Project Pitch

- There is a need for rapid deployment of negative emissions
- Incentives are currently insufficient
- In northern Europe, biomass and forestry waste are important domestic fuels.
- In Europe as a whole, the use of waste-derived fuels seems destined to increase.
- Difficult to convert, being inhomogeneous and rich in problematic ash species.
- In the Bio-Flex CLC project the ambition is to devise a technology which can convert difficult fuels in “CFB”-mode or “CLC”-mode.

Bio-Flex CLC partners
RISE RESEARCH INSTITUTE OF SWEDEN
CHALMERS TEKNISKA HOGSKOLA
SPANISH NATIONAL RESEARCH COUNCIL
TECHNISCHE UNIVERSITAT DARMSTADT
AICHERNIG ENGINEERING
BABCOCK & WILCOX VOLUND AB
NATIONAL CERTH CENTER FOR RESEARCH AND TECHNOLOGICAL DEVELOPMENT
1CUBE
FORTUM POWER AND HEAT POLSKA
VÄXJÖ ENERGI AB

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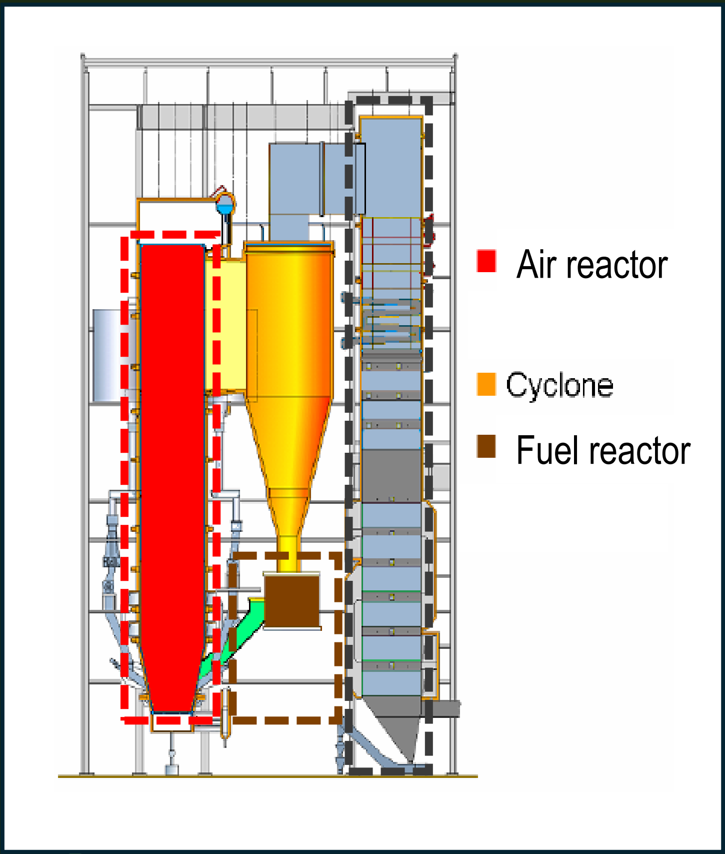
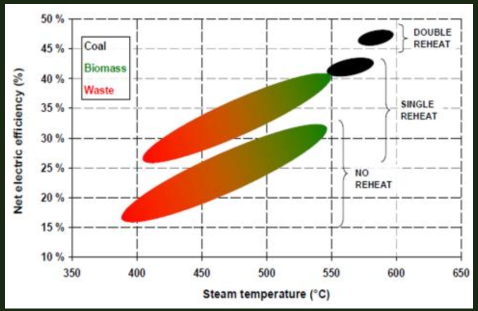
Bio-Flex CLC Project Pitch



- The CFB-CLC system takes advantage of the similarities between conventional CFB and CLC.
- We argue that we can design a system which can be operate in two main modes
  - CLC with CCUS
  - CFB without CCUS

Important to consider that a Flexible CFB-CLC system is basically a conventional CFB with an added reactor (FR) on the return side

Would provide end-users with lower economic and technical risk



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Project Activities

- Demonstration CFB-CLC at 1 MW scale with at least three relevant domestic fuels.
- Work on pilot and lab scale related to fuel conversion pathways and ash chemistry. This includes development of new methods of improving fuel conversion.
- Down stream treatment and CO2 liquefaction for Bio-Flex CLC.
- Process evaluation and optimization of BioFlex-CLC.
- Sustainability analysis and social life cycle analysis of Bio-FlexCLC

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Bio-Flex CLC

Questions / Comments