## 4 Presentations from the project: Biomass Combustion Chemistry with Oxygen Carriers

- Ash components and oxygen carriers, main challenges, Henrik Leion
- Gas-phase alkali interactions with reactor walls and OC in a laboratory reactor, Viktor Andersson
- Alkali emissions measurements in continuous CLC operation, Ivan Gogolev
- CLC with K, Na impregnated charcoal in a batch fluidizedbed reactor, Daofeng Mei



# Biomass Combustion Chemistry with Oxygen Carriers

- Energy technology, Chalmers
- Department of Chemistry & Molecular Biology, University of Gothenburg
- Energy and Material, Chalmers



# Ash components and oxygen carriers, main challenges

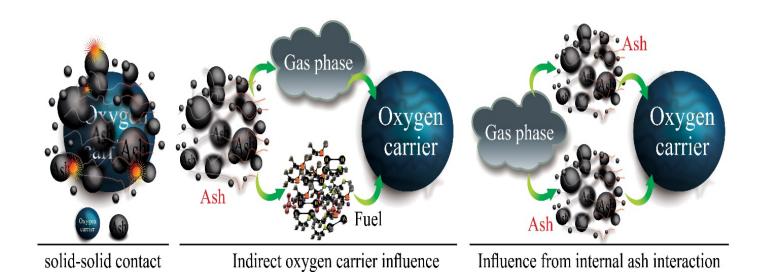
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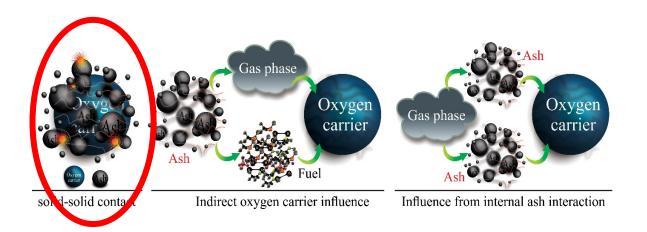


## Outline of this presentation:

- General mechanism on oxygen carrier ash interaction with known examples
- Example of results on oxygen carrier ash interaction in fixed bed
- Challenges with oxygen carrier ash interaction

## Suggestions for main mechanisms.



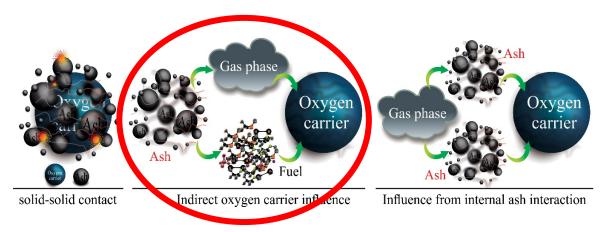


#### Examples:

Quartz and clay minerals generally don't react with the oxygen carrier Keller et al. Chem. Eng. Research and Design 92, 2014

Fe<sub>2</sub>O<sub>3</sub> or CaSO<sub>4</sub> can add oxygen carrier ability Rubel et al., Fuel, 88, 2009; Bao, Applied Energy 115, 2014

CaO can form a shell on carriers (but without affecting reactivity)
Azis, Chem. Eng. & Technology 36, 2013

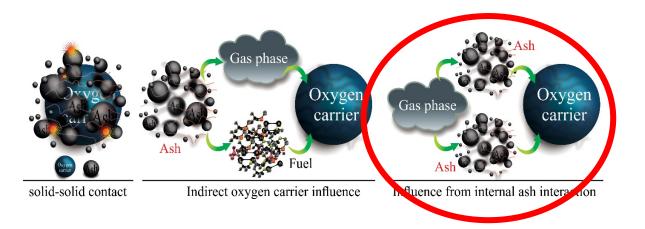


#### Examples:

K penetrating ilmenite accelerating Ti-Fe separation Knutsson et al. Applied Energy 157, 2015

K enhances gasification Keller et al. Combustion and Flame 158, 2011

CaO enhances water-gas-shift reaction Teyssié et al. Energy and Fuels 25, 2011



#### Examples:

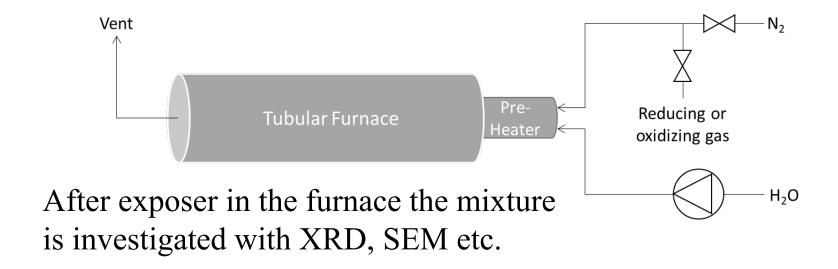
Alkali creates melts with SiO<sub>2</sub>

P + K can, more or less, block the oxygen carrier Hildor et al. ACS Omega 5, 2020; Störner et al. Energy and Fuels 34, 2020

P + Ca can, more or less, block the oxygen carrier Staničić et al. Chem. Eng. Research and Design 149, 2019

### Fixed bed experiment:

Oxygen carriers are mixed with ashes or ash components (salts)



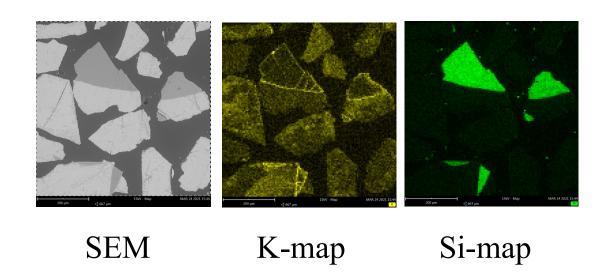
Fixed bed provides high solid-solid contact (worst case scenario)

Easy to compare different cases

Simple to compare with thermodynamic data

#### Cross sections of partials casted in epoxy

Ilmenite (with sand) mixed with K<sub>2</sub>SO<sub>4</sub>
Reducing condition H<sub>2</sub> in H<sub>2</sub>O, 900°C



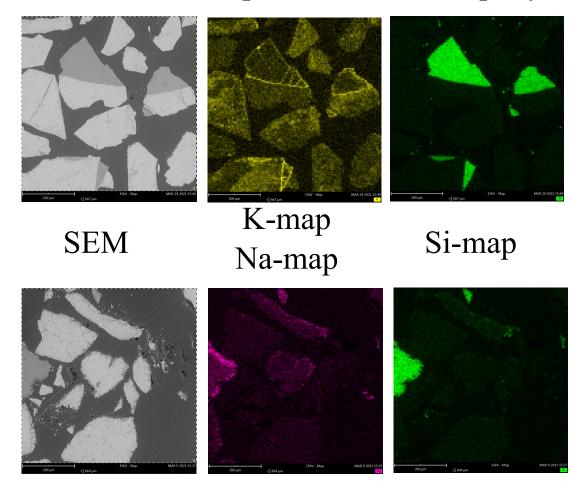
Ilmenite absorbs K just as well or better than sand

#### Cross sections of partials casted in epoxy

Ilmenite (with sand) mixed with K<sub>2</sub>SO<sub>4</sub>

Reducing condition H<sub>2</sub> in H<sub>2</sub>O, 900°C

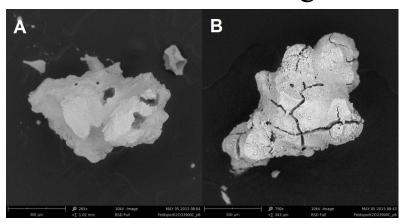
Ilmenite (with sand) mixed with Na<sub>2</sub>SO<sub>4</sub>



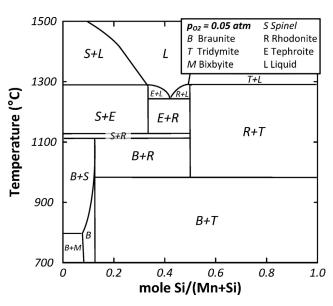
Ilmenite absorbs K but Na stays on the surface

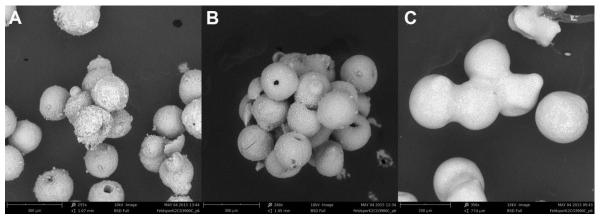
Unpublished results

#### Overview SEM images



Sand mixed with K<sub>2</sub>CO<sub>3</sub> Mn<sub>3</sub>O<sub>4</sub> mixed with K<sub>2</sub>CO<sub>3</sub>





Reducing condition H<sub>2</sub> in H<sub>2</sub>O, 850°C

94%wt  $Mn_2O_4$  6%wt  $SiO_2$  75%wt  $Mn_2O_4$  25%wt  $SiO_2$  90%wt  $Mn_2O_4$  10%wt  $SiO_2$ 

Leion et al. 25<sup>th</sup> EUBCE, 2017

### Challenges with oxygen carrier ash interaction

Ash is generated in the fuel reactor, hence reducing conditions are most relevant. (similar to gasification but with solid oxygen present)

Conventional combustion ash is generated in the presence of air (similar to OCAC, CLOU or the air reactor)

Trends from conventional ash chemistry might not hold since ash components can interact with the metal oxide.

Impurities in the oxygen carrier might be just as important

A strategy for depleted oxygen carriers is needed

Measuring ash component and is challenging

We have a lot of different Oxygen Carriers and several of different ashes

 $\begin{array}{cc} \text{CuO/Cu}_2\text{O/Cu} & & \\ \text{FeTiO}_3/\text{Fe}_2\text{TiO}_5+\text{TiO}_2 \end{array}$ 

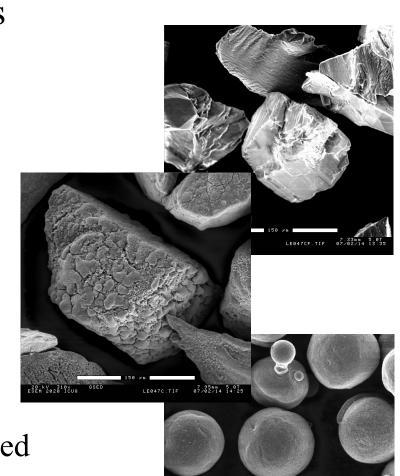
 $MnFeO_3/(MnFe)_3O_4$ 

NiO/Ni

Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>/FeO/Fe

CaMnO<sub>3</sub>/CaMnO<sub>3-8</sub>

Vassilev et al. (Fuel, 208, 2017) presented 141 different ash compositions (some were mean values)



## Thank you for your attention!

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