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CuO as an Oxygen Carrier for Direct Solid Fuel Chemical Looping Combustion

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Outline

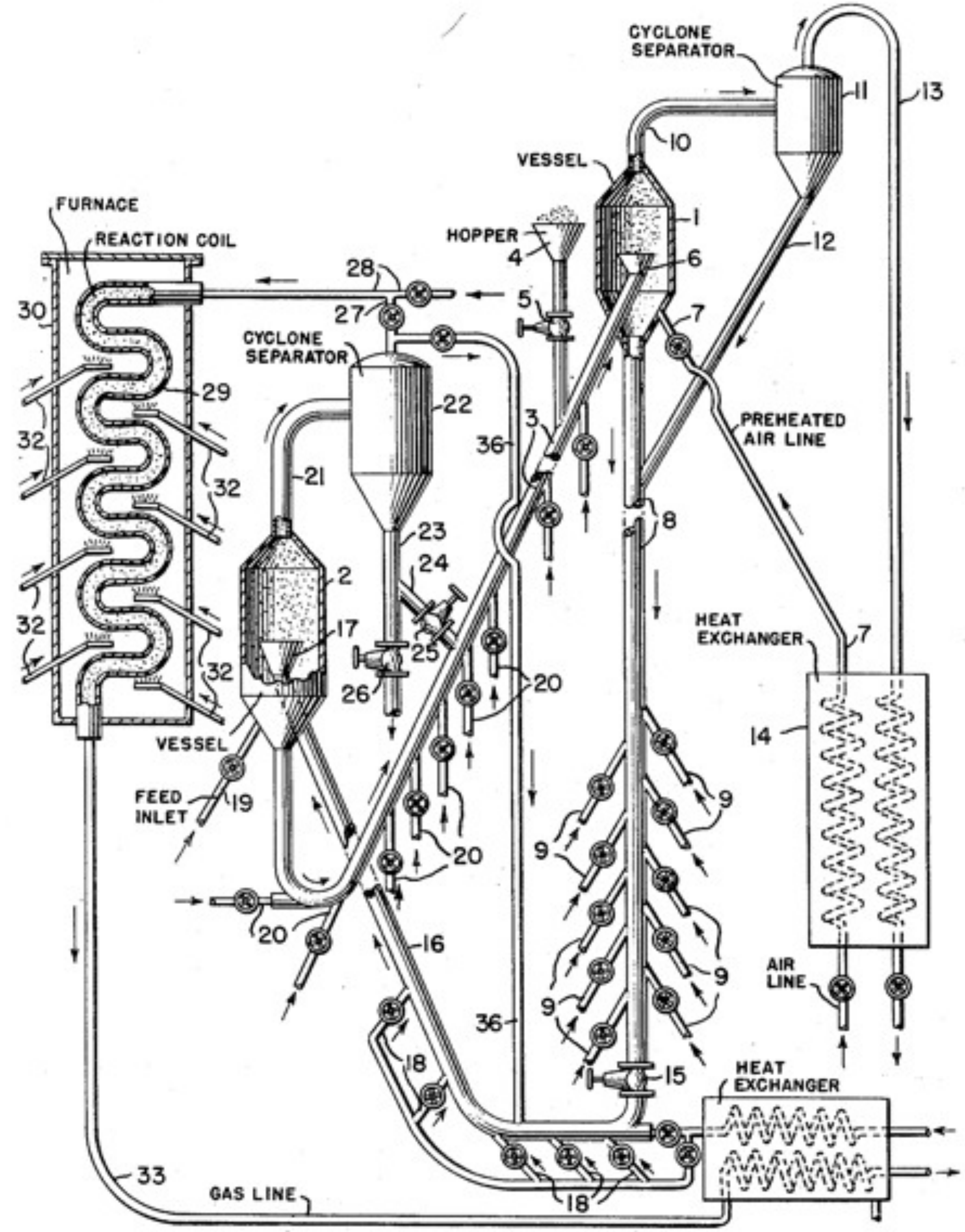
- History of chemical looping
- Chemical looping combustion configurations
- Copper as a CLOU carrier
- Kinetics of a copper-based CLOU system
- System design considerations
- Conclusions

Early History

Patent filed by by Gilliland in 1946 (awarded 1954):

"Production of industrial gas comprising carbon monoxide and hydrogen"

"a metal as oxygen carrier, … first reacted with air to produce an oxide, then … reacted with the hydrocarbon to … carbon monoxide and hydrogen" "finely divided metal oxide … in a fluidized state"

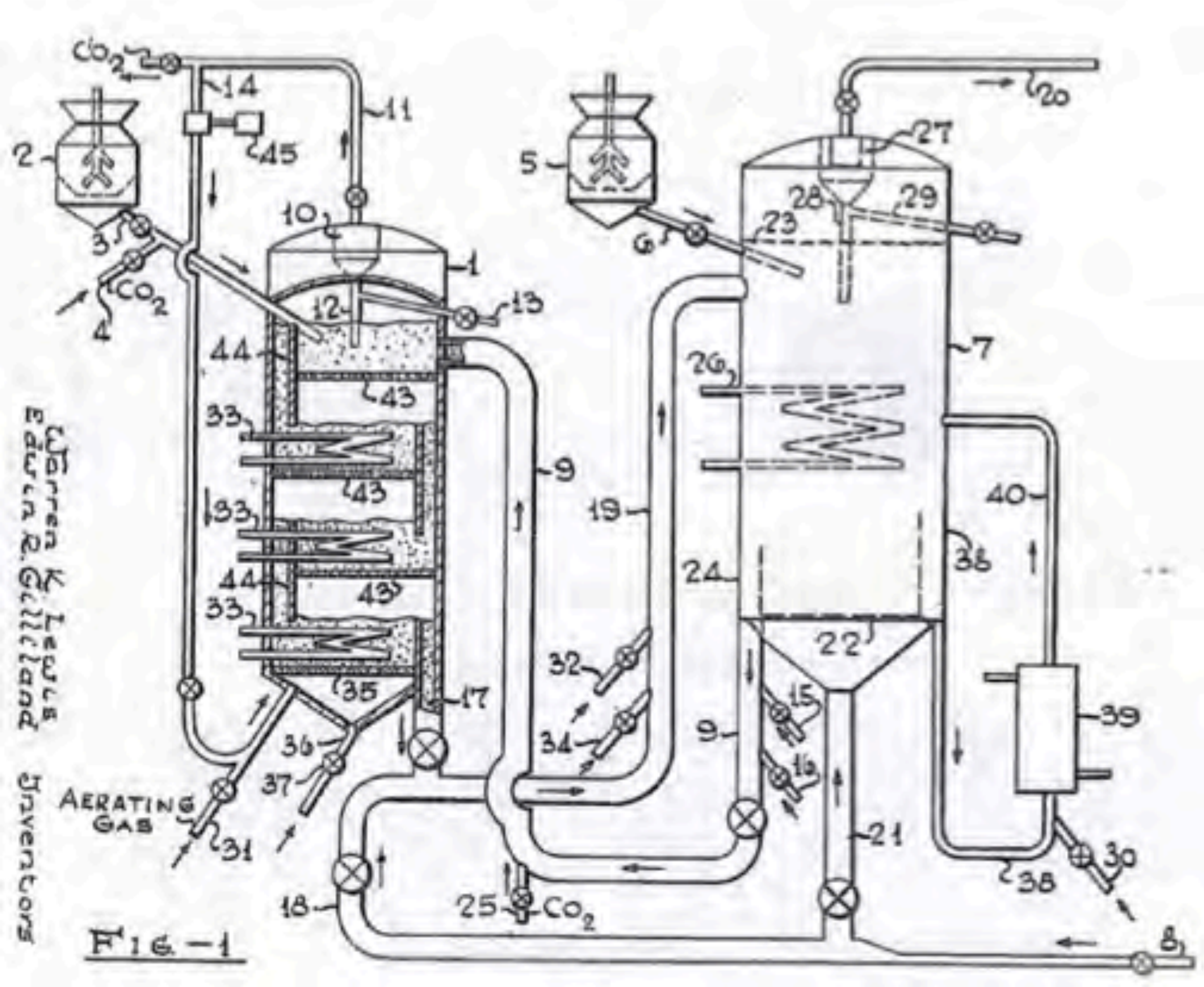


Early History (cont.)

Patent filed by Lewis and Gilliland in 1950 (awarded 1954):

"Production of pure carbon dioxide"

using a "solid oxygen carrier" using "any oxidizable carbonaceous material", such as charcoal, coal, coke.... natural gas.... lignite... using two interconnected fluidized beds



Other Notable Dates

1983 Thermodynamic study by Richter & Knoche: "Reversibility of Combustion Processes" proposing the principle of CLC to increase efficiency

1987 Thermodynamic study by Ishida introduces the name "Chemical-Looping Combustion"

1994 Ishida proposes the use of CLC for CO_2 capture

2000 Lyon proposes "Unmixed combustion" for solid fuels, including experimental data

2003 >100 h of operation in 10 kW unit at Chalmers

2005 Patent application by Chalmers for CLOU (Chemical Looping with Oxygen Uncoupling)

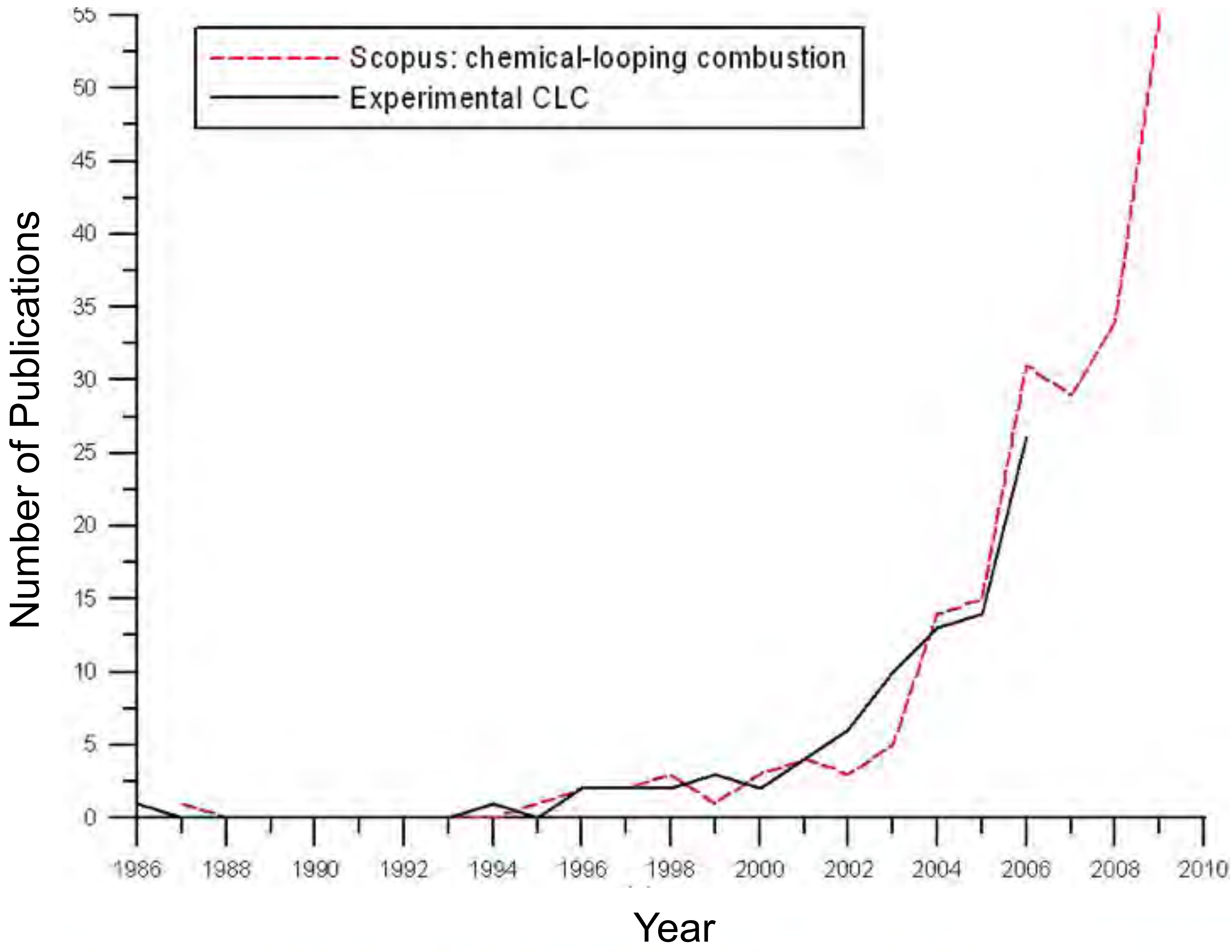
2006 Solid fuel CLC in continuous operation, Chalmers

2008 120 kW dual CFB operated in Vienna

2010 1st International Conference on Chemical-Looping, in Lyon

2010 Fan publishes "Chemical Looping Systems for Fossil Energy Conversions"

Publications on Chemical Looping Combustion



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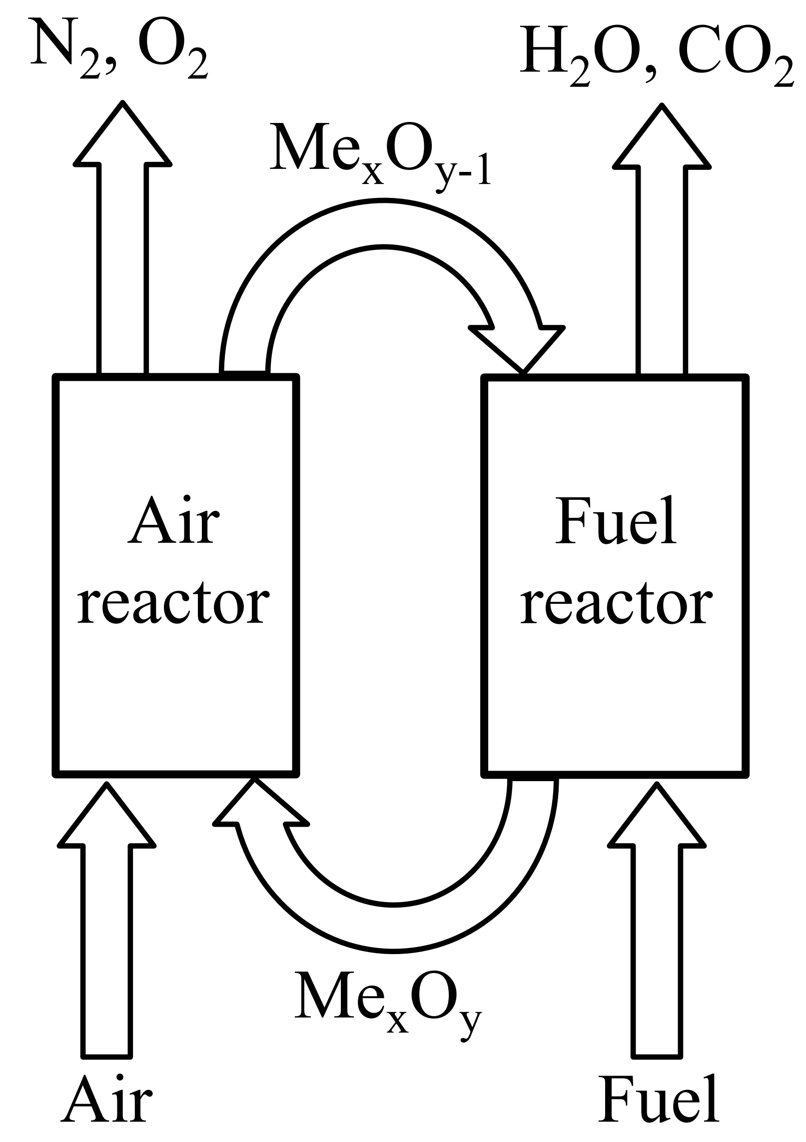
CLC with Gaseous Fuel

Air Reactor:

$\frac{1}{2} O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$

Fuel Reactor:

$CH_4 + 4\, Me_xO_y \rightarrow Me_xO_{y-1} + 2\, H_2O + CO_2$



(Indirect) CLC with Solid Fuel

Air Reactor:

$$\tfrac{1}{2} O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$$

Fuel Reactor:

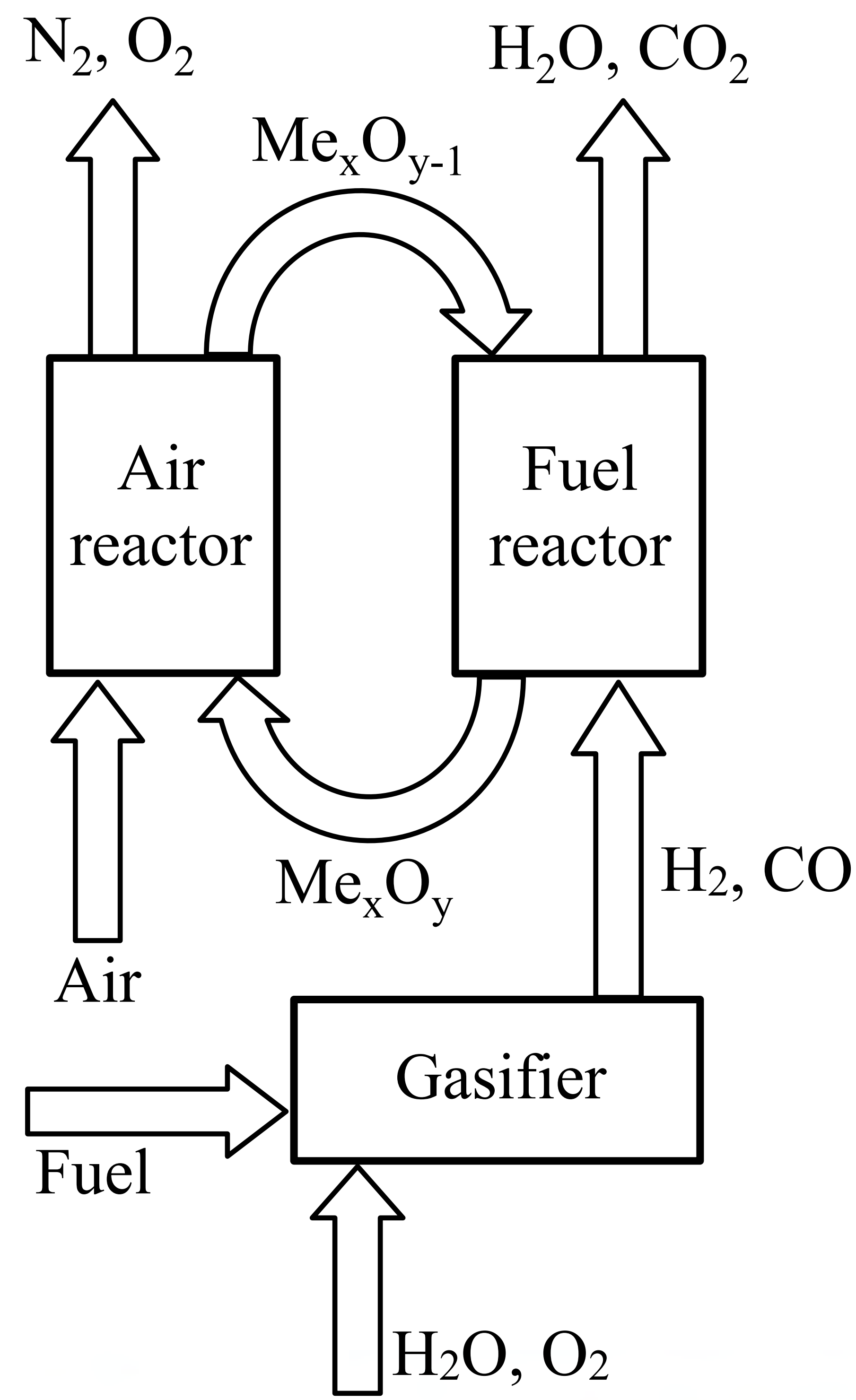
$$CO + Me_xO_y \rightarrow Me_xO_{y-1} + CO_2$$

$$H_2 + Me_xO_y \rightarrow Me_xO_{y-1} + H_2O$$

Gasifier:

$$C + H_2O \rightarrow H_2 + CO$$

$$C + \tfrac{1}{2} O_2 \rightarrow CO$$



(Direct) CLC with Solid Fuel

Air Reactor:

$\frac{1}{2}\,O_2 + Me_xO_{y-1} \rightarrow Me_xO_y$

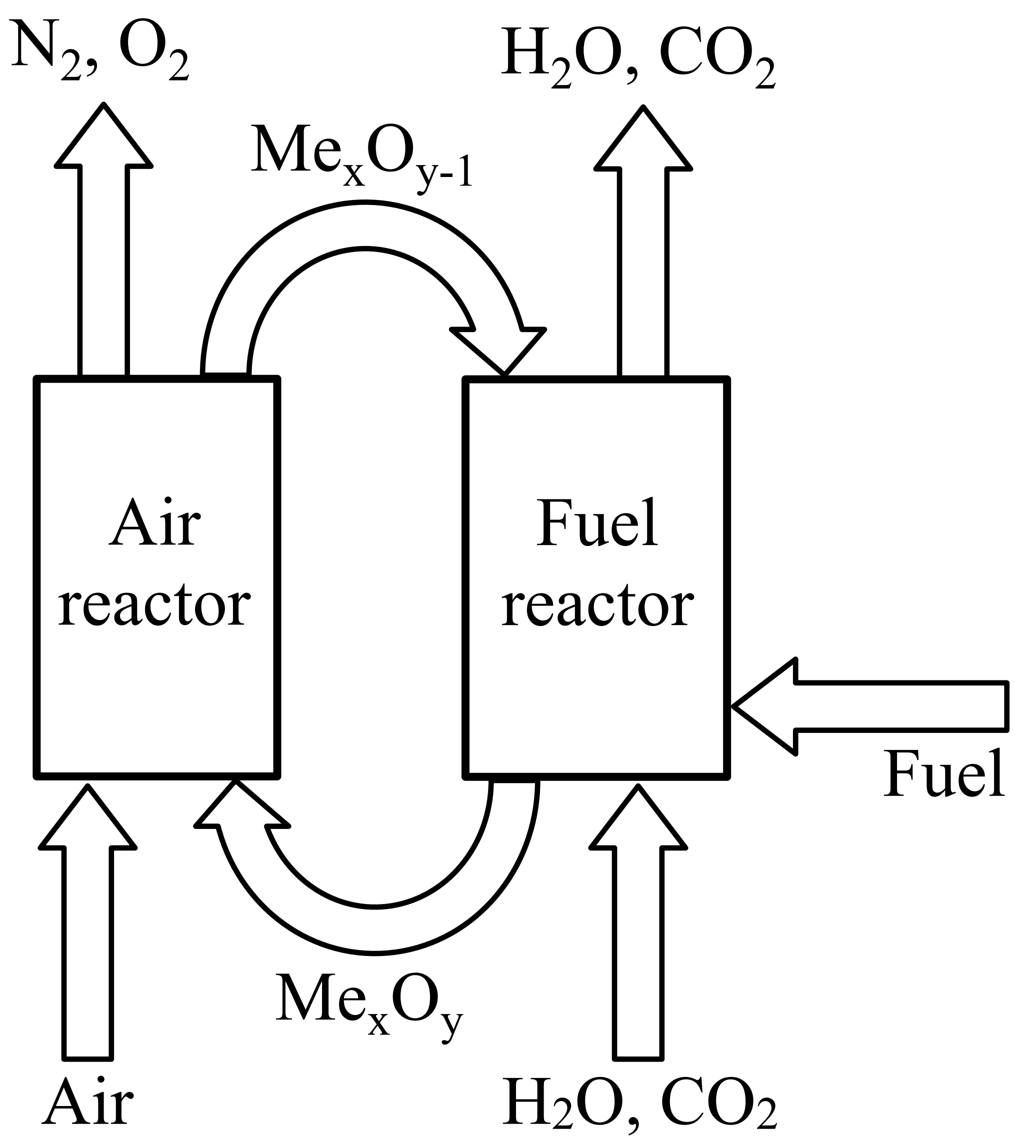
Fuel Reactor:

$C + H_2O \rightarrow H_2 + CO$

$C + CO_2 \rightarrow 2\,CO$

$CO + Me_xO_y \rightarrow Me_xO_{y-1} + CO_2$

$H_2 + Me_xO_y \rightarrow Me_xO_{y-1} + H_2O$



CLOU with Solid Fuel
(Chemical Looping with Oxygen Uncoupling)

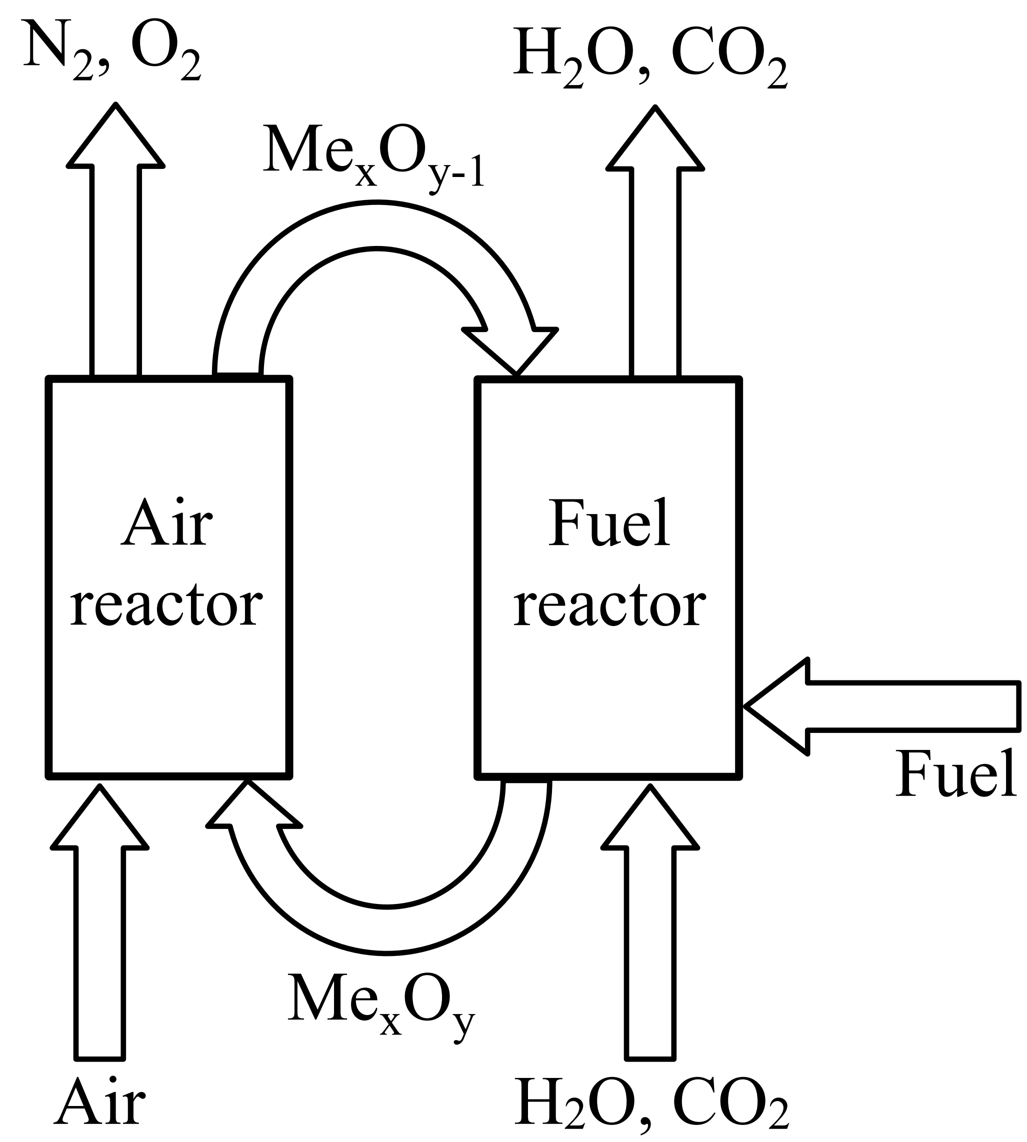
Air Reactor:

$\frac{1}{2} O_2 + Me_xO_{y-1} \leftrightarrow Me_xO_y$

Fuel Reactor:

$Me_xO_y \leftrightarrow Me_xO_{y-1} + \frac{1}{2} O_2$

$C + O_2 \rightarrow CO_2$



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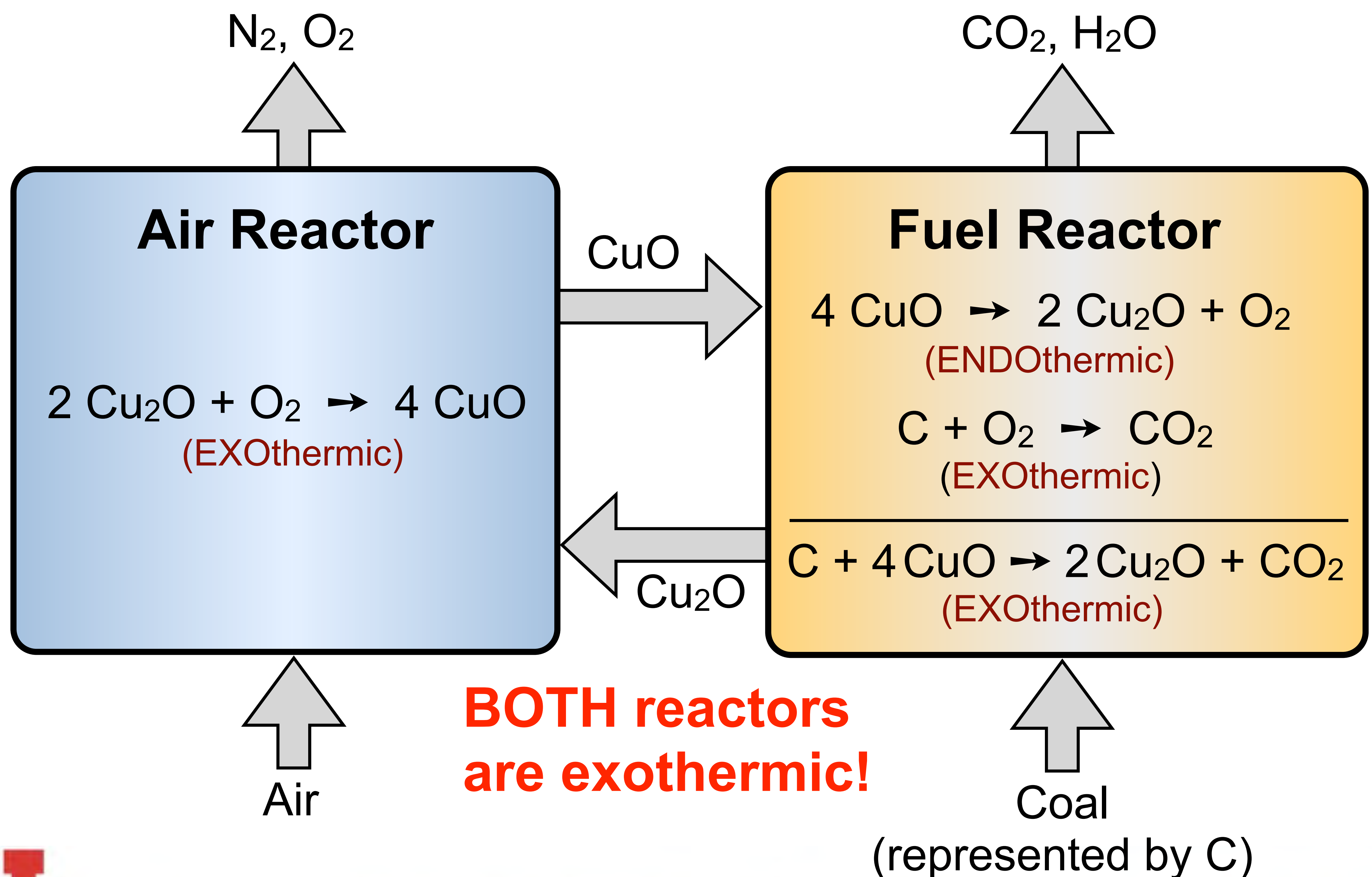
Why Does CLOU Work?

$$2\,Cu_2O(s) + O_2(g) \leftrightarrow 4\,CuO(s)$$

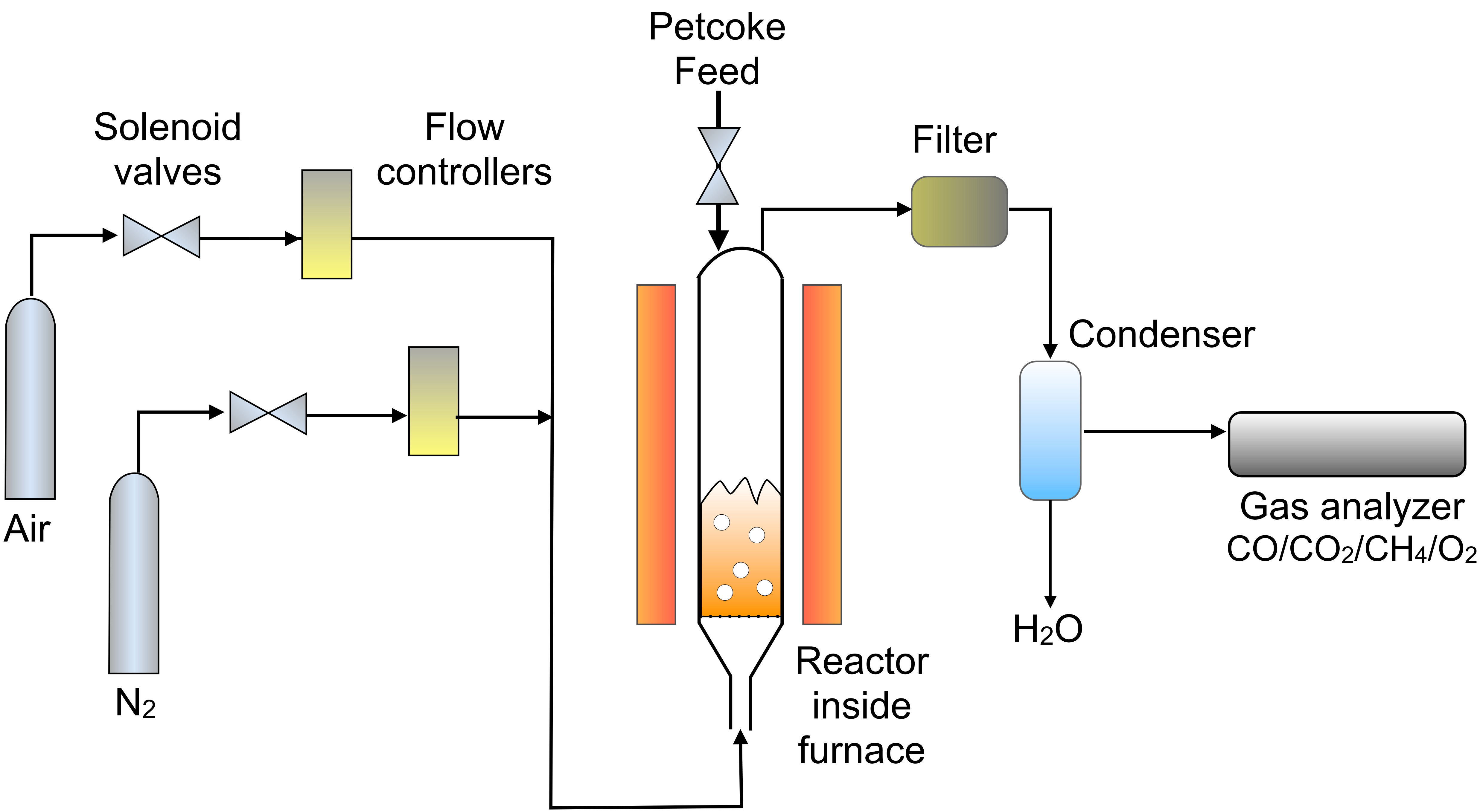
- Thermodynamics
  - At higher temperatures, equilibrium of the metal oxidation reaction is pushed "towards the left"
  - Equilibrium partial pressure of O_2 is appreciable at combustion temperatures
- Reactor system configuration
  - Air reactor has relatively high concentration of O_2, which forces the reaction above to the right
  - Fuel reactor has low concentration of O2 (since it is rapidly consumed by the fuel), pushing the above reaction to the left
- Only a few metal/metal oxide combinations that exhibit CLOU behavior in a reasonable temperature range have been identified

Copper-Based CLOU

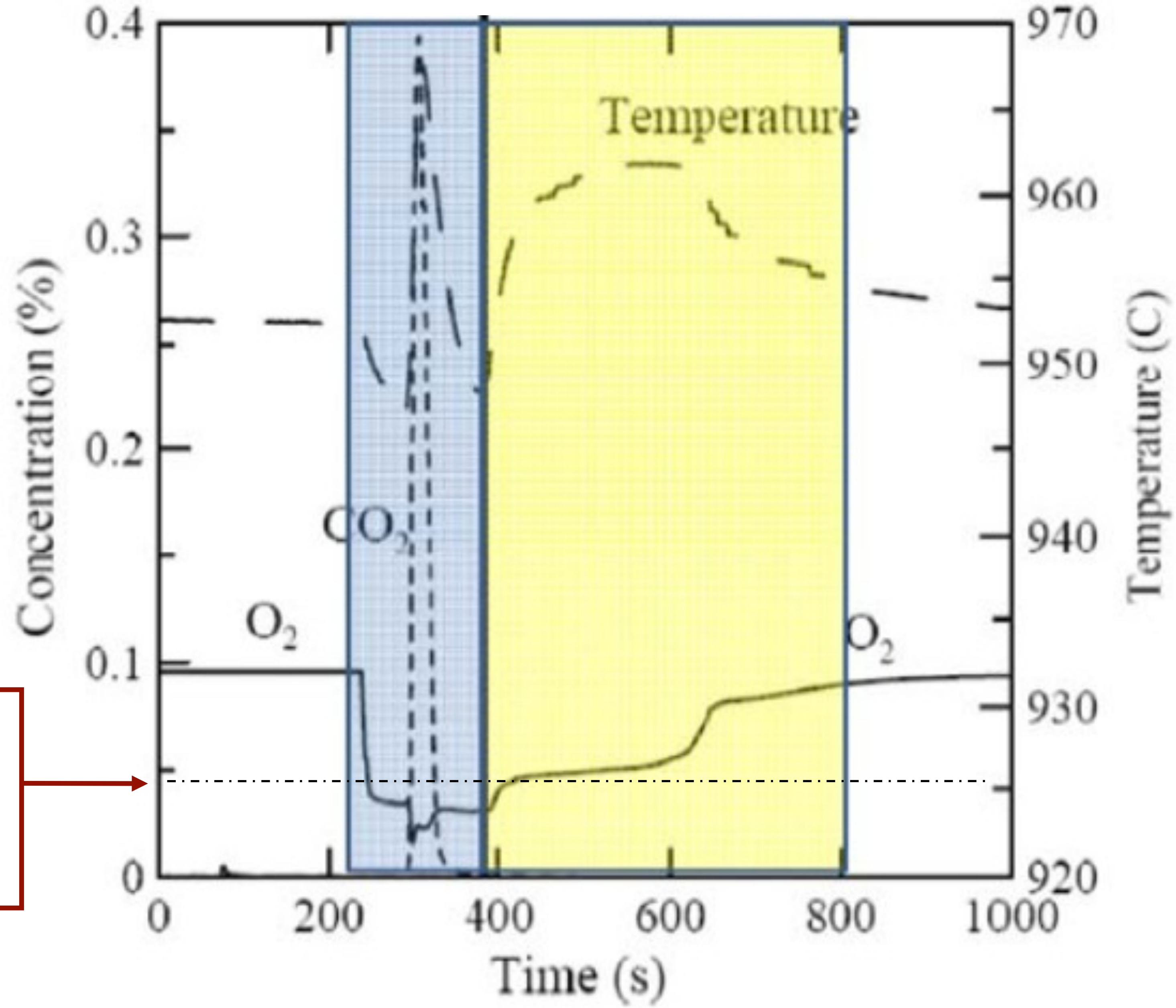


Fluidized Bed CLC System

(Setup used by Mattisson, 2009)



CLOU Combustion of Petcoke at 955°C
(Mattisson, 2009)



Equilibrium Partial Pressure of O_2 (0.0455 atm.)

Figure adapted for interpretation from Mattisson T., Leion H., Lyngfelt A. (2009) Chemical-looping with oxygen uncoupling using CuO/ZrO_2 with petroleum coke, *Fuel* ***88, 683-690.***

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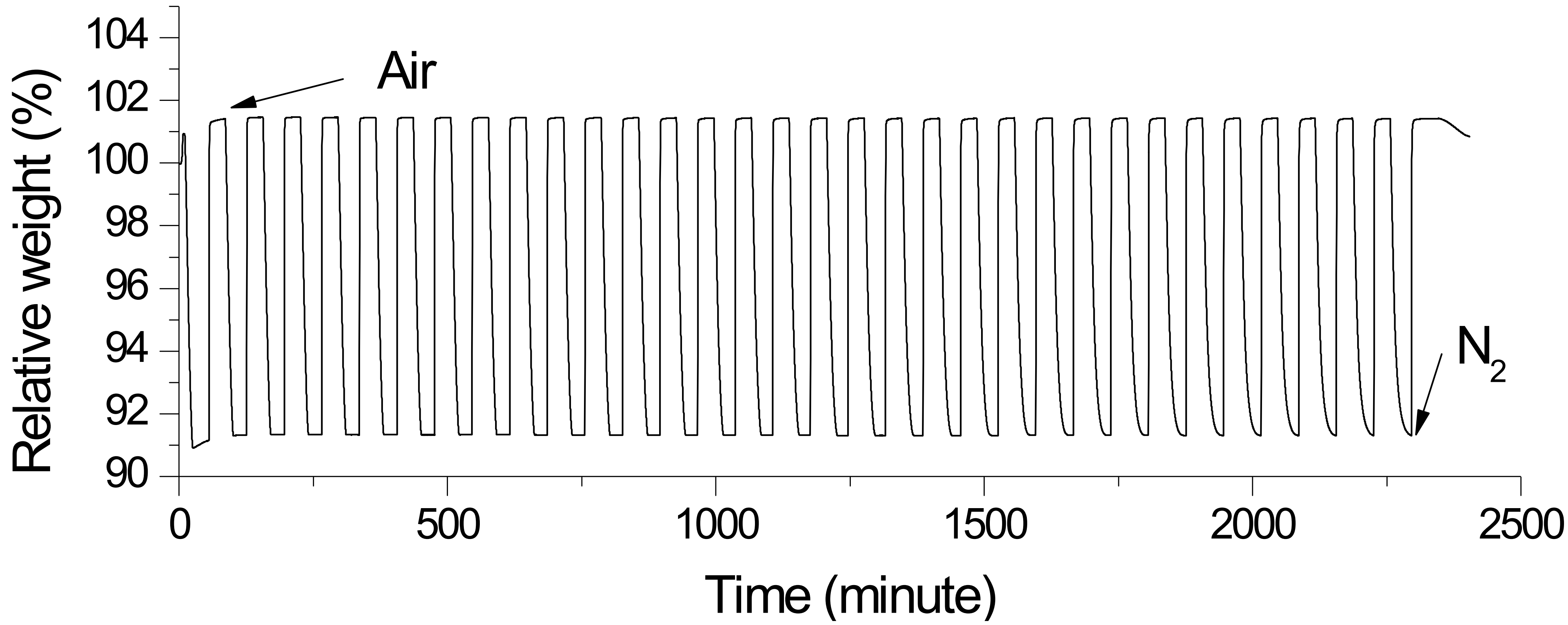
CLOU Oxidation-Reduction Cycling

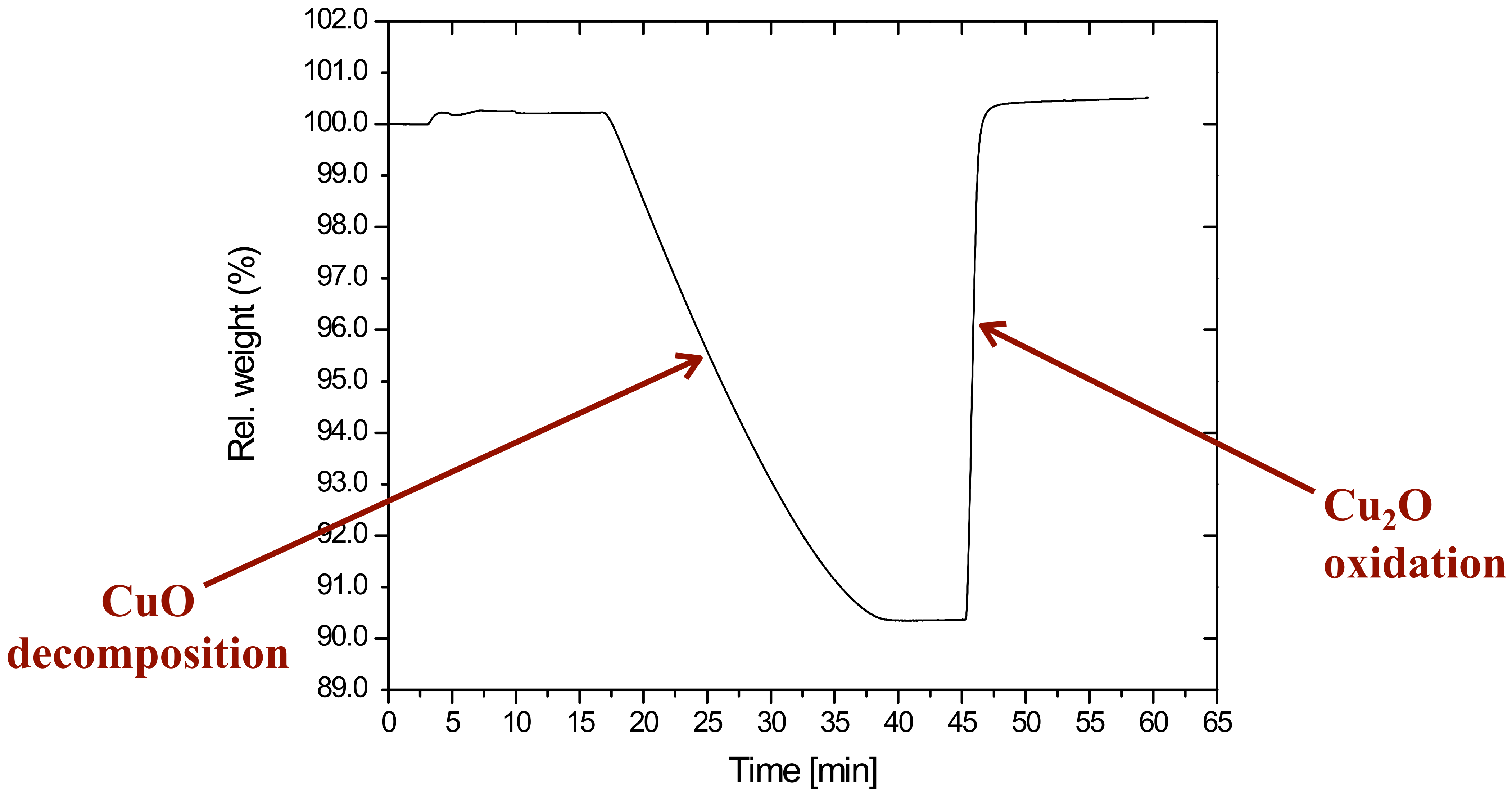
Cycling atmosphere to TGA between air (30 min) and nitrogen (40 min) at 850°C to determine stability of CuO as an oxygen carrier.



Results suggest that CuO decomposes to Cu_2O based on weight loss (~10%)

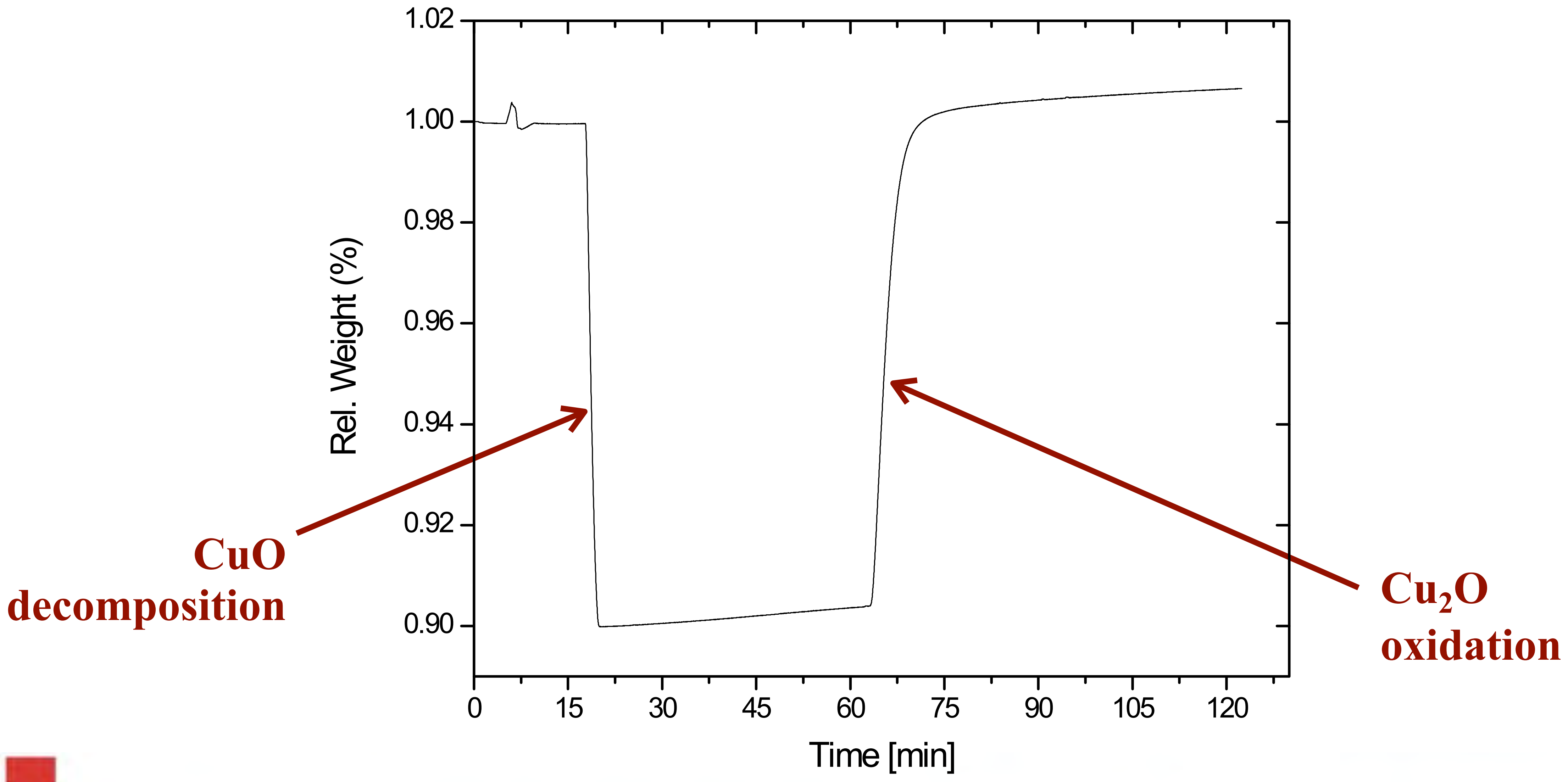
Rates at 850°C

Isothermal 850°C
(one cycle: nitrogen for 40 minutes and air for 30 minutes)

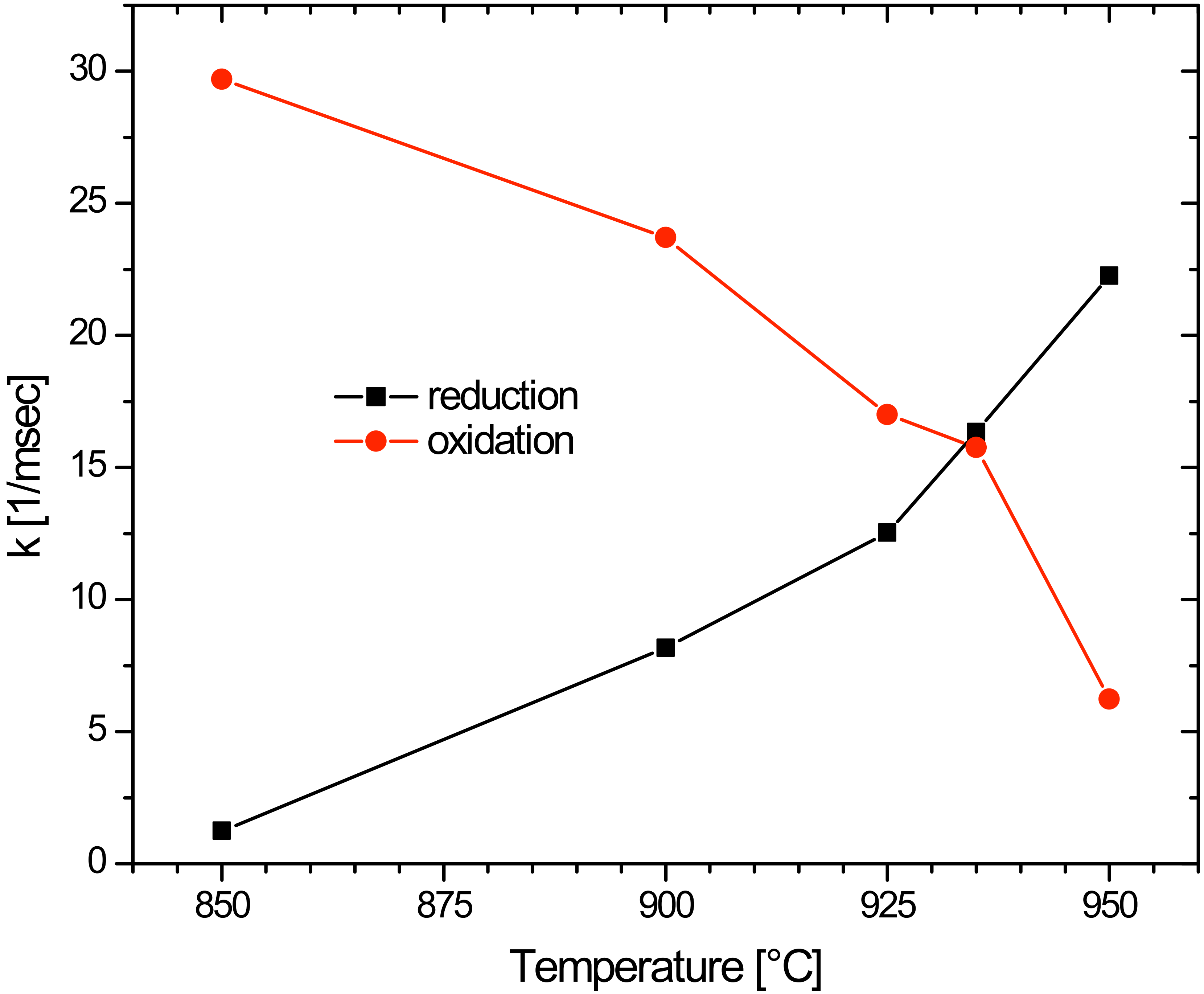


Rates at 950°C

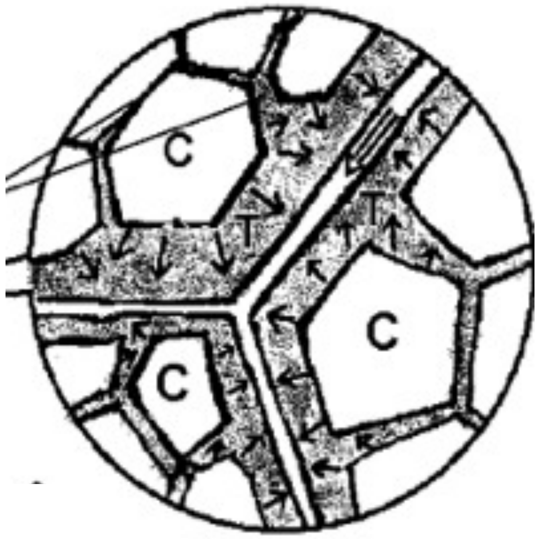
Isothermal 950°C
(one cycle: nitrogen for 40 minutes and air for 30 minutes)



Rate Constants for CuO Decomposition and Cu_2O Oxidation in Air



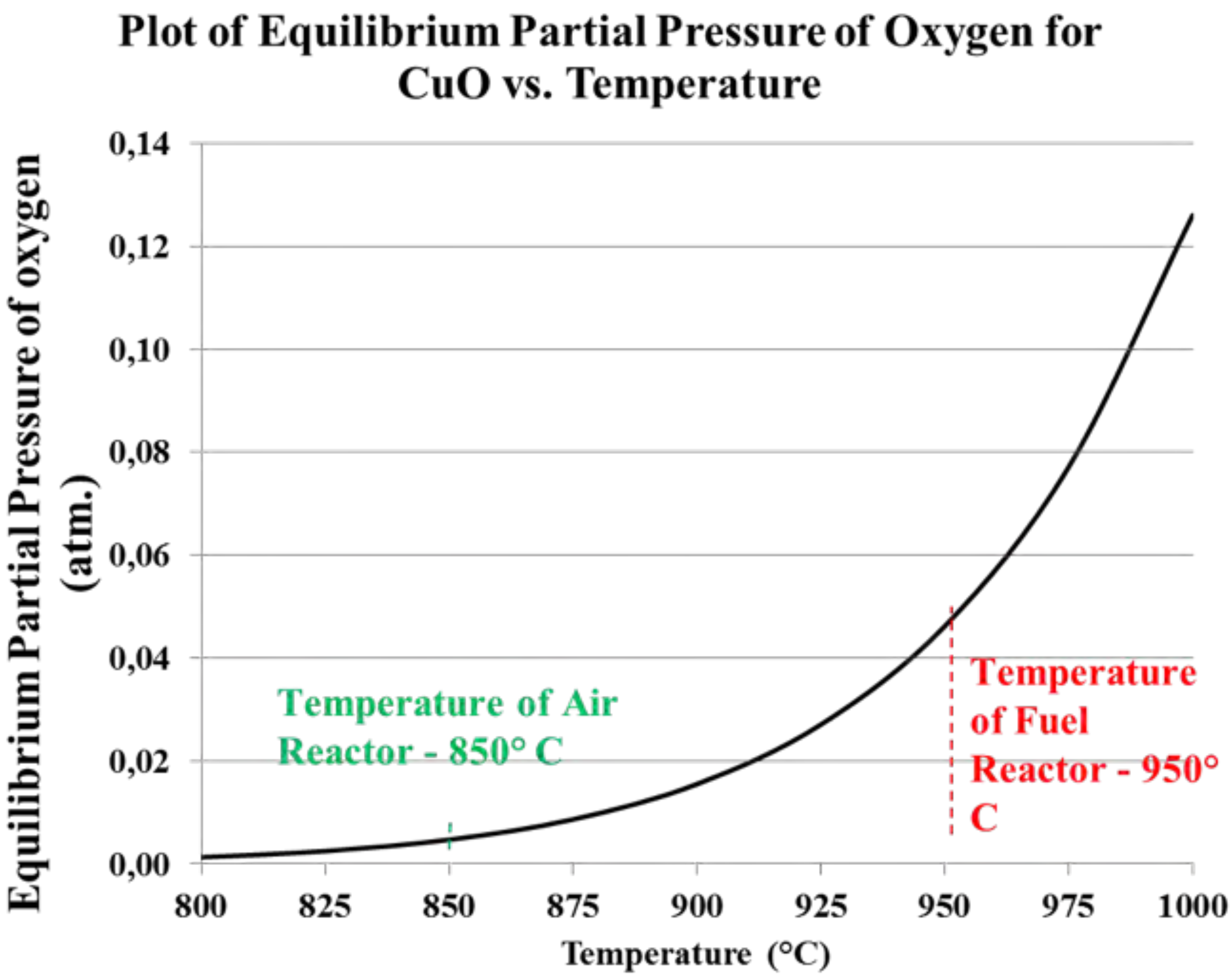
Prisedsky & Vinogradov: Cu_2O grains surrounded by fractured CuO



Zhu, Minura, and Isshiki:

"The activation energy becomes..negative due to sintering of CuO grains" and decrease in grain boundary diffusion

Selection of Temperatures for Air and Fuel Reactors

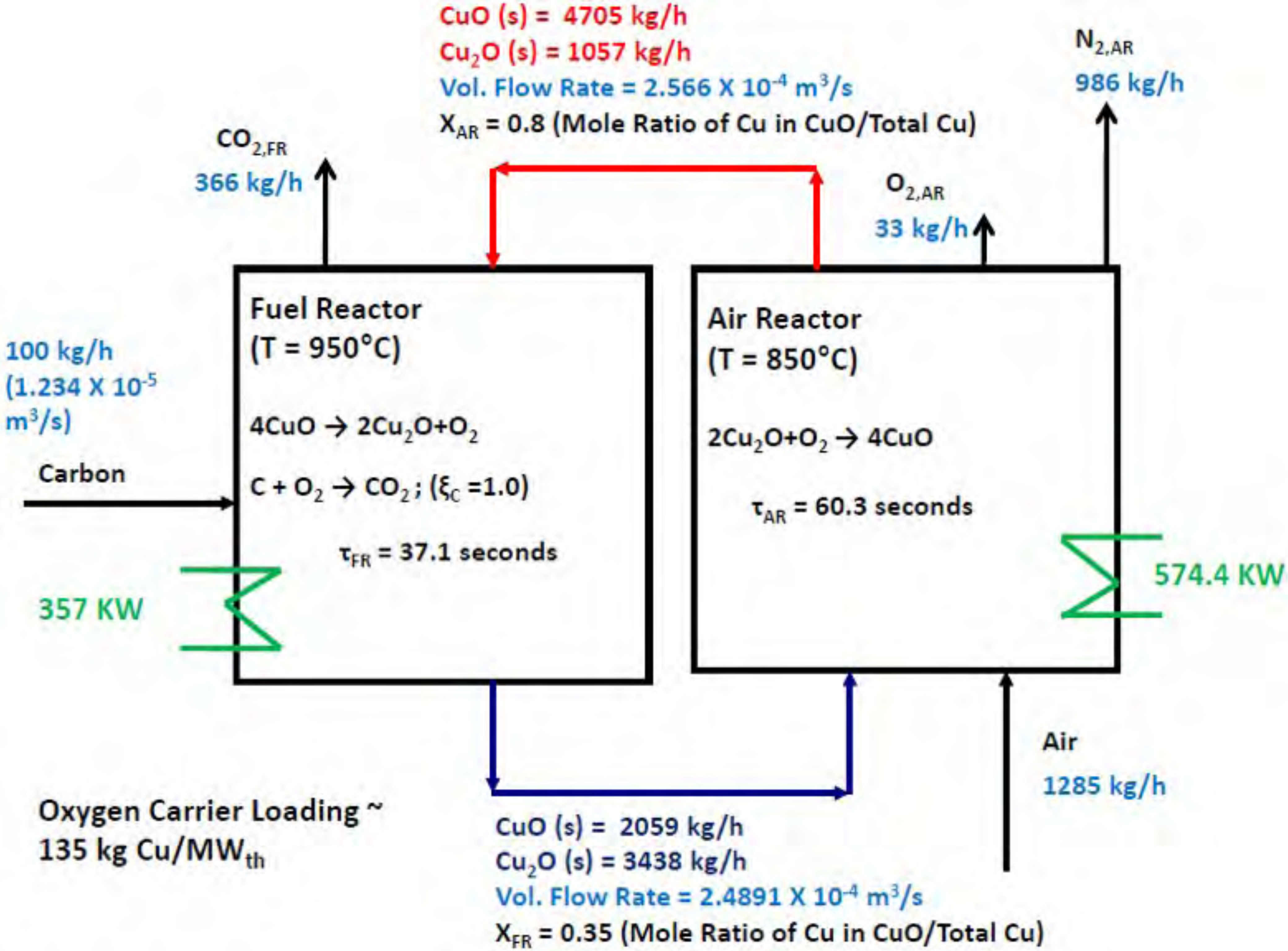


For air reactor rate is a maximum at ~ 850°C

For fuel reactor rate increases with T but agglomeration is a concern above ~ 950°C

System Modeling

(Basis: 100 kg/h carbon input)



Research at University of Utah

- Carrier development and characterization
  - Production
    - Support material selection
    - Copper addition technique
    - Degree of copper loading
    - Particle formation technique
  - Characterization
    - Carrier capacity
    - Oxidation and reduction kinetics
    - Fluidized bed performance (kinetics, attrition, sintering, agglomeration)
- System modeling and simulation
  - Process balances
  - Fluidized bed simulations
- Process development and evaluation
  - New 100 kWth CLOU process development unit at off-campus laboratories

Conclusions

- Chemical looping with oyxgen uncoupling (CLOU) an attractive technology for processing of solid fuels with inherent isolation of CO_2
- CuO/Cu_2O an efficient oxygen carrier system for CLOU combustion process
- Rate of O_2 release increases with temperature
- Rate of oxidation decreases with temperature due to decrease in grain boundary diffusion
- Sintering/agglomeration of CuO at combustion temperatures requires that carrier be supported

Acknowledgements

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