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

Kevin J. Whitty

Department of Chemical Engineering
Institute for Clean and Secure Energy
The University of Utah
Salt Lake City, Utah, USA
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 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”
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 CO₂ 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

![Graph showing the number of publications on Chemical Looping Combustion over the years. The graph compares the number of publications as categorized by Scopus and as Experimental CLC. The number of publications has increased significantly from the late 1980s to the early 2010s.](image-url)
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
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:
\[ \frac{1}{2} O_2 + Me_{xO_{y-1}} \rightarrow Me_{xO_y} \]

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:
\[ C + H_2O \rightarrow H_2 + CO \]
\[ C + \frac{1}{2} O_2 \rightarrow CO \]
(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:
\[
Me_xO_y \leftrightarrow Me_xO_{y-1} + \frac{1}{2} O_2
\]
\[
C + O_2 \rightarrow CO_2
\]
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
Why Does CLOU Work?

$2 \text{Cu}_2\text{O}(s) + \text{O}_2(g) \leftrightarrow 4 \text{CuO}(s)$

• Thermodynamics
  – At higher temperatures, equilibrium of the metal oxidation reaction is pushed “towards the left”
  – Equilibrium partial pressure of $\text{O}_2$ is appreciable at combustion temperatures

• Reactor system configuration
  – Air reactor has relatively high concentration of $\text{O}_2$, which forces the reaction above to the right
  – Fuel reactor has low concentration of $\text{O}_2$ (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

**Air Reactor**

\[ \text{N}_2, \text{O}_2 \]

\[ 2 \text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4 \text{CuO} \quad \text{(EXOThermic)} \]

**Fuel Reactor**

\[ \text{CO}_2, \text{H}_2\text{O} \]

\[ 4 \text{CuO} \rightarrow 2 \text{Cu}_2\text{O} + \text{O}_2 \quad \text{(ENDOThermic)} \]

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad \text{(EXOThermic)} \]

\[ \text{C} + 4 \text{CuO} \rightarrow 2 \text{Cu}_2\text{O} + \text{CO}_2 \quad \text{(EXOThermic)} \]

Air

CuO

Cu\textsubscript{2}O

Both reactors are exothermic!

Coal

\( \text{represented by C} \)
Fluidized Bed CLC System
(Setup used by Mattisson, 2009)
CLOU Combustion of Petcoke at 955°C (Mattisson, 2009)

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.
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
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$_2$O based on weight loss (~10%)
Rates at 850°C

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

CuO decomposition

Cu₂O oxidation
Rates at 950°C

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

CuO decomposition

Cu₂O oxidation
Rate Constants for CuO Decomposition and Cu$_2$O Oxidation in Air

Prisedsky & Vinogradov: Cu$_2$O 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)

CuO (s) = 4705 kg/h
Cu₂O (s) = 1057 kg/h
Vol. Flow Rate = 2.566 × 10⁻⁴ m³/s
X_{AR} = 0.8 (Mole Ratio of Cu in CuO/Total Cu)

CO₂,FR
366 kg/h

Fuel Reactor
(T = 950°C)
4CuO → 2Cu₂O + O₂
C + O₂ → CO₂ ; (ξ₀ = 1.0)
τ_{FR} = 37.1 seconds

N₂,AR
986 kg/h

O₂,AR
33 kg/h

100 kg/h
(1.234 × 10⁻⁵ m³/s)
Carbon

357 KW

Air Reactor
(T = 850°C)
2Cu₂O + O₂ → 4CuO

τ_{AR} = 60.3 seconds

574.4 KW

Oxygen Carrier Loading ~ 135 kg Cu/MWₜₐₜ

CuO (s) = 2059 kg/h
Cu₂O (s) = 3438 kg/h
Vol. Flow Rate = 2.4891 × 10⁻⁴ m³/s
X_{FR} = 0.35 (Mole Ratio of Cu in CuO/Total Cu)

Air
1285 kg/h
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 oxygen uncoupling (CLOU) an attractive technology for processing of solid fuels with inherent isolation of CO₂

• CuO/Cu₂O an efficient oxygen carrier system for CLOU combustion process

• Rate of O₂ 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

• This material is based upon work supported by the Department of Energy under Award DE-NT0005015

• Tobias Mattisson, Henrik Leion and Anders Lyngfelt (Chalmers University)

• Adel Sarofim (Univ. Utah)

• Chris Clayton, Gabor Konya, Asad Sahir (Univ. Utah)