Oxygen Carrier Development for Chemical Looping Combustion Of Methane and Coal

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Oxygen Carrier Development

- Oxygen carrier development is critical for the CLC process

- Challenges
  - High oxygen transfer capacity
  - High reaction rates
  - High attrition resistance
  - Stable performance during multi cycle tests at high temperature
  - No agglomeration
  - Scaling up the manufacturing process
Oxygen Carrier Selection

- Pure metal oxides and supported metal oxides have been previously investigated.
  - $\text{Fe}_2\text{O}_3$, CuO, NiO, and Mn$_3$O$_4$

- $\text{Fe}_2\text{O}_3$ and Mn$_3$O$_4$
  - Inexpensive
  - Low reactivity

- CuO
  - High reactivity
  - Exothermic reaction
  - Agglomeration issues due to low melting point

- NiO
  - High reactivity
  - Environmental concerns

- **NETL Research**
  - Mixed metal oxides for improving the reaction performance
  - Bi metallic and tri metallic oxygen carriers
CuO-Fe$_2$O$_3$ Oxygen carrier development

- Lab scale preparations for both coal and methane CLC
- Worked with an industrial partner Nexceris Inc. to prepare 500 lb (227 kg) batches with two different particle sizes
- Bench scale CLC tests for performance evaluation with methane and coal
- Pilot scale methane CLC tests


*Applied Energy 183 (2016) 1550–1564*

*Applied Energy, 107 (2013), 111–123*

*Fuel, 108 (2013), 319–333*


*U.S. Patent 9,523,499 B1, Dec. 20 , 2016*
Experimental Methods
Thermo-Gravimetric Analysis (TGA)

*Methane CLC*

- Initial evaluation of reactivity with mg level quantities
  - Heat the solid in the TGA pan to reaction T
  - Introduce methane for isothermal reaction

- Measure weight change as a function of time

- Fractional Reduction \(X = \frac{(M_0 - M)}{(M_0 - M_f)}\),
  \[M = \text{Instantaneous weight}\]
  \[M_0 = \text{Initial weight}\]
  \[M_f = \text{Final weight}\]

- Compute rate data using the weight change data
  
  *Global rates of reactions \((dX/dt)\) were calculated by differentiating fractional conversions \((X)\)*
TGA Comparative Data of Methane CLC with CuO-Fe$_2$O$_3$-Al$_2$O$_3$ and hematite at 800 °C - 20% methane/N$_2$ (10 min)/air (30 min)

- Significantly higher rate and oxygen transfer capacity than that with hematite
- Hematite only reduces to Fe$_3$O$_4$
- Total weight change of 15.2 wt.% corresponds to further reduction to Fe$^0$ and Cu$^0$
- Synergy effects - Deeper reduction of iron oxide in the presence of Cu
- Stable performance during 50 cycle test
• **Temperature programmed reductions (TPR)**
  – Ramp temperature (20°C/min) from ambient to up to 1000 °C in 16.6% CH$_4$

• **Simultaneous Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) during TPR**

• **TGA**
  – Global rates of reactions (dX/dt) were calculated by differentiating fractional conversions (X)

• **DSC**
  – Identification of exothermic and endothermic reactions
Comparisons of CuFe$_2$O$_4$ Temperature programmed reactions in DSC/TGA with methane with single Metal OC

- CuO and Fe$_2$O$_3$ - initiate reactions above 700 °C & maximum rate above 800 °C
- CuO-Fe$_2$O$_3$ mixtures - initiate reaction around 600 °C & maximum around 800 °C
  - Reaction T is significantly lower
- Synergy effects of Fe-Cu is observed during reactions with methane
Chemical Looping Combustion of Methane with commercially prepared spray dried oxygen carriers:

500 lb (227 kg) - Particles size 50 to 250 μ

- Worked with an industrial partner Nexceris Inc. to prepare 500 lb (227 kg) batches
- Bench scale CLC tests for performance evaluation with methane and coal
- Pilot scale methane CLC tests
Spray Dried CuO-Fe$_2$O$_3$-Al$_2$O$_3$ Synthetic Oxygen Carrier
Commercially prepared at Nextech
227 kg batch, Particle size - 50 to 250 µ

- Composition - 30 wt.% CuO, 30 wt.% Fe$_2$O$_3$ and 40 wt.% Alumina
- Particle density – 2.49 g/cm$^3$
- Skeletal density – 4.7 g/cm$^3$
- Bulk density - 1.43 g/cm$^3$
- Surface area – 12 m$^2$/g
- Heat capacity – 2.9 J/kg C @ 800 C
Reaction Performance Evaluation

*Bench Scale Fluidized Bed Test with Methane/air at 800 °C*

- 5.5cm ID with a heated reaction zone of 91.4 cm
- Oxygen carrier bed height was 25.4 cm
- Reduction – 10 vol.% CH\(_4\)/10%Ar/N\(_2\)
- Oxidation – air
- Purge gas - 7L N\(_2\) between oxidation-reduction cycles
- 25 cycle test
Bench Scale Fluidized Bed Tests - 25 Cycle Methane CLC Test at 800 °C

Comparative data of CuO-Fe₂O₃-Al₂O₃ and natural mineral hematite

- Reduction: 15 & 75 minutes with 10 vol.% CH₄/10%Ar/N₂ & Oxidation – air
  Umf - 0.4 SLPM (0.73 cm/s), Flow rate -14 Umf, Weight - 1600g
- Methane conversion and the oxygen transfer capacity values for the CuO-Fe₂O₃-Al₂O₃ are significantly higher than that for the hematite: Estimated reduction to FeO/Fe⁰/Cu⁰
- 90 % conversion of methane can be achieved using this oxygen carrier
- No agglomeration even with copper
- Stable reactivity
Experimental Methods

- 3 air jets, 380 microns each
- Air flow rate: 10 L/min
- Gas velocity: ~300-400 m/s
- 5-hour test, fines are collected and weighed after 1st, 2nd & 5th hours
- Attrition Index % = Total fines collected/Initial Mass
Attrition data comparisons of CuO-Fe$_2$O$_3$-Al$_2$O$_3$ prepared by spray dried method (50 to 250 µ) and the standard

- Attrition resistance was better than that with standard material
- Attrition resistance was acceptable for pilot scale tests
Heats of reaction of methane
30 wt.% CuO-30 wt.% Fe\textsubscript{2}O\textsubscript{3} -40 wt.% Alumina

Theoretical calculations using Facts Age

- CuO-Fe\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} reduction is exothermic above 600 °C
- Consistent with DSC data
- Exothermic reduction reaction is advantageous
- Minimal heat transfer necessary from the oxidizer
Pilot scale tests with CuO-Fe$_2$O$_3$-Al$_2$O$_3$

**NETL’s 50kW$_{th}$ Integrated CL Reactor**

- **Fuel Reactor**
  - Bubbling fluidized bed
  - 20 cm inside diameter
- **Air Reactor**
  - Turbulent fluidized bed
  - 15 cm inside diameter
- **L-Valve, Riser, and Dip-legs**
  - 5 cm inside diameter (nominal)

**Key Design Parameters**

1) No external heat addition to the solids flow path
2) Self-sustaining operation is possible if heat released = heat loss
NETL’s 50kW\textsubscript{th} Integrated CL Reactor

*Test parameters with CuO-Fe\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} oxygen carrier (50 to 250 \(\mu\))*

- **Fuel**
  - Natural gas
- **Operating Pressures**
  - 1 – 2 bar (current test campaigns)
- **Solids circulation rates**
  - 50 – 400 kg/hr
- **Solids inventory**
  - 50 – 75 kg
- **Operating Temperatures**
  - 700 – 1000 °C
Netl’s 50 kWth Integrated CL Reactor

Methane to CO₂ Conversion of CuO-Fe₂O₃-Al₂O₃ (50 to 250 µ) as a Function of Fuel Concentration (balance N₂)

- Heat management in the fuel reactor was excellent due to the exothermic reaction of CuO and methane

- Solid agglomeration issues traditionally observed at high CuO concentrations (>15% wt) were not observed

- The variations in the fuel conversions are due to the discrete operating variables: methane concentration, flow rates, temperature and carrier circulation rate

- Methane conversions to CO₂ as high as 80–90% can be achieved with the oxygen carrier

- Particle losses from cyclones and fast solid transfer due to high flow rates
Chemical Looping Combustion of Methane with commercially prepared CuO-Fe$_2$O$_3$-Al$_2$O$_3$

*Tumbling method -solid state mixing, Particles 170 -582 microns*
CuO-Fe₂O₃-Al₂O₃ Synthetic Oxygen Carrier
Commercially Prepared by tumbling Method
500 lb. (227 kg) batch, Particle size range – 177-582 µm

- Composition - 30 wt.% CuO, 30 wt.% Fe₂O₃ and 40 wt.% Alumina
- Heat Capacity – 2.9 J/(kg*C) @ 800C
- Particle density – 2.9 g/cm³
- Bulk density – 1.85 g/cm³
- Skeletal Density – 4.73 g/cm³
Fluidized bed reactor test data at 800 °C and attrition data comparisons of CuO-Fe$_2$O$_3$-Al$_2$O$_3$ prepared by tumbling method (170 -582µ) and spray dried method (50 to 250 µ).

- Reduction – 15 mins. & 5 mins. with 20 vol.% CH4/20%Ar/N2
- Oxidation – air, MFV 800 C - 0.0317 m/s & 0.135 m/s, Flow rate – 3 & 1.2 X Umf, Weight – 925 & 1000g

- Stable reactivity was observed with 170 -582µ particles
- Attrition resistance was acceptable
NETL 50kWth Chemical Looping Reactor (CLR) – with 177-582 μ particles

- System was modified to include secondary cyclones
- Secondary cyclones were added to capture fines and un-attrited materials that escape from the reactor.
SAM-NETL 50kW$_{th}$ CLR- Conversion of methane to CO$_2$ during the CLC sections with 177-582 µm particles

- Temperature and residence times were varied during CLR operation
- Methane Conversion to CO$_2$: 33.9% - 76.5%
- Increase in conversion with increasing temperature as expected
- Regions with larger variations are due to the changes in solid inventory
Particle size analysis data of fresh and after the pilot scale test with 177-582 μ particles

- Particle losses with bigger particles from tumbling method were less than that with spray dried particles
- Losses are due to attrition, system upsets and transport disintegration due to the design of the system
- Particle size distribution of particles collected from the reactor after the test was similar to that of the fresh
Scanning electron photomicrographs of fresh and after the pilot scale test with 177-582 µ particles

- Fresh particles have a rough surface
- After the pilot test some particles had similar morphology to the fresh but some had smoother surface
- Possible loss of outer layer of particles remained in the reactor for a long time
Pilot Scale Test Summary with 177-582 µm particles

- Easier operation with bigger particles than that with smaller particles for the current system design
- It was possible to achieve more than 40 hours of chemical looping operation
- At some conditions, the unit was operating without adding external heat to the process: complete auto-thermal
  - CuO-Fe₂O₃-Al₂O₃ has exothermic reaction in the fuel reactor
- No agglomeration even though the copper concentration was 30 wt.% and oxygen carrier was able to withstand high temperatures up to 950 °C.
- Good solid circulation, good methane conversion and good heat management, stable operating regimes at relatively low inventories and low circulation rates
- Methane Conversion in CLR can be improved by:
  - Optimizing fuel reactor design (higher bed and inventory)
  - Adding steam with the natural gas
- Solid loss was less with bigger particles possibly due to low physical/chemical stress
Coal CLC
Fluidized bed tests of coal CLC with synthetic CuO-Fe₂O₃-Al₂O₃

*Temperature programmed reactions*

- Reactor height of is 35.4 cm, and the diameter is 6 cm.
- Coal and OC were mixed: coal-10g to oxygen carrier-322g
- The mixture was heated from 25 to 850 °C in Argon at flow rate of 11.7X Umf
- 30 vol.% steam was introduced at 300 or 850 °C
- Sample was cooled to 750 °C to initiate oxidation with air
Fluidized Bed CLC Tests of Wyodak Coal with CuO-Fe$_2$O$_3$-Al$_2$O$_3$

Comparative data of coal/steam/oxygen carrier and blank coal/steam

Temperature ramp from ambient to 850°C in 30% steam

- Rapid increase in production of CO$_2$ and fast consumption of CO and H$_2$
- Total carbon oxides production was more with the coal/oxygen carrier
  - Oxygen carrier promotes gasification/combustion
  - Complete combustion of coal

Coal + steam produces syngas
- Syngas reacts with oxygen carrier
Reactions of Wyodak coal with Oxygen from CLOU
Steam introduction at 850 °C

- When Coal was heated in He to 850 °C without steam there was no CO and H2 production until steam was introduced at 850 °C
- When coal/Cu-Fe oxygen carrier was heated even without steam substantial amount of CO₂ was observed
- Oxygen from CLOU participates in the combustion reaction
Summary

• Mixed metal oxide oxygen carriers showed better reactivity and stability

• Commercial preparations of and CuO-Fe₂O₃-Al₂O₃ were successful

• NETL’s 50-kW th chemical looping circulating fluidized bed combustor unit with the commercially prepared oxygen carrier showed very promising results with both particle sizes
  – Good heat management
  – Easy solid transfer
  – High methane conversion
  – No agglomeration of solid at 900 °C even though the oxygen carrier had 30% CuO
  – Better operation with larger particles prepared by tumbling method

• Promising results with bench scale coal CLC tests
  – Future pilot plant tests planned with coal
How Does Cu Promote the Extent of Reduction of Fe$_2$O$_3$ with Coal and Methane?

**High Reactivity with bi-metallic**
- Cu enhances deeper reduction of iron oxide and stable performance during multi cycle test
- Similar observations reported methane reforming reactions (previously reported)
- CuFe$_2$O$_4$ has a tetragonally distorted spinel structure Fe$^{3+}$[Fe$^{3+}$Cu$^{2+}$]O$_4$
  - Octahedral cations are placed inside the square bracket
- During reduction it is known to form defective structure and cracking in the micro structure
  - Enhances the methane gas transfer facilitating Fe$_2$O$_3$ reduction.
- Cu-O and Fe-O bond energies are different from that in CuFe$_2$O$_4$

**No Agglomeration Issues**
- Agglomeration issues with CuO was not observed with CuO-Fe2O3
- Both Fe$^{3+}$ and Cu$^{2+}$ distributed uniformly
- Well dispersed Cu with Fe minimizes agglomeration of Cu
  - Metallic Cu and FeO/Fe$_3$O$_4$ are immiscible