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Combustion of Coal Using Chemical Looping Oxygen Carriers

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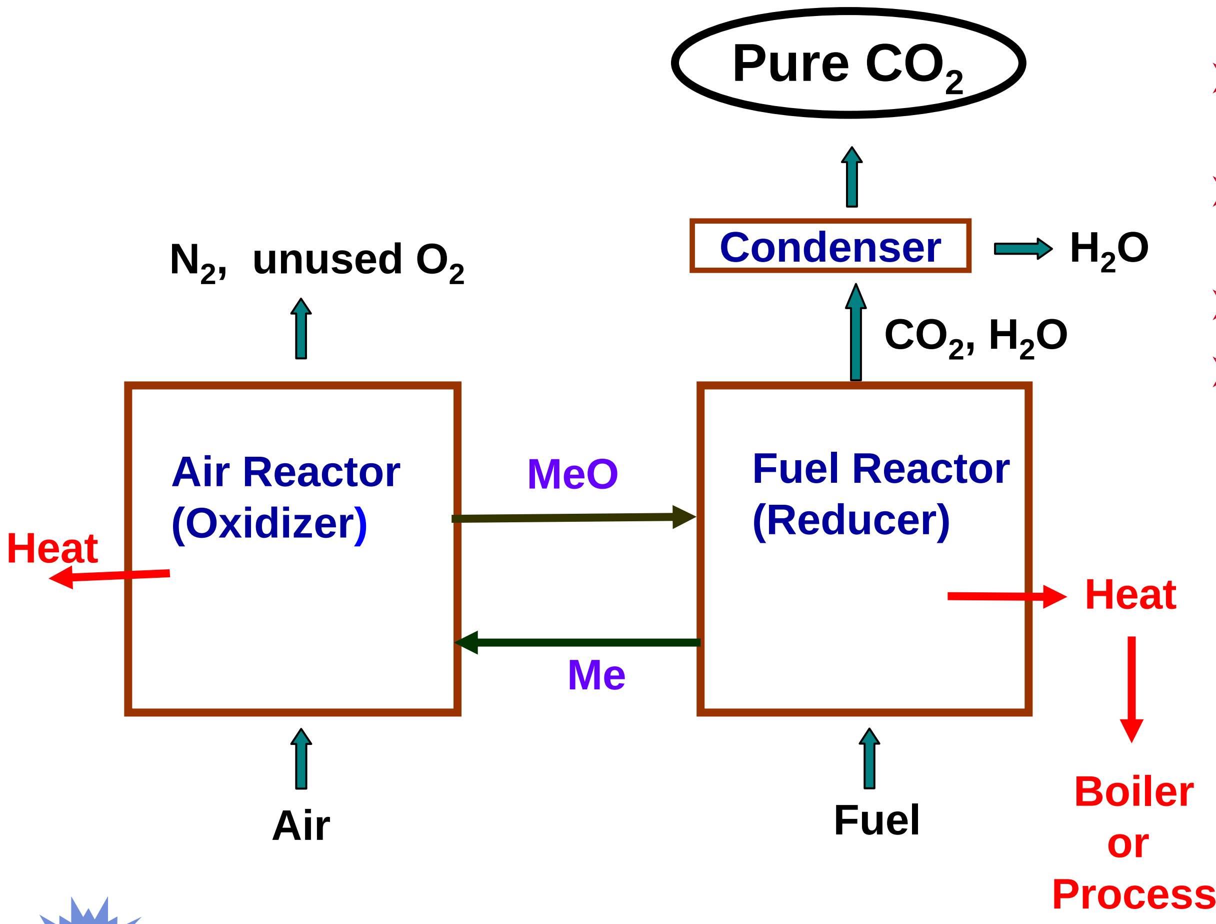
Introduction

Chemical Looping Combustion

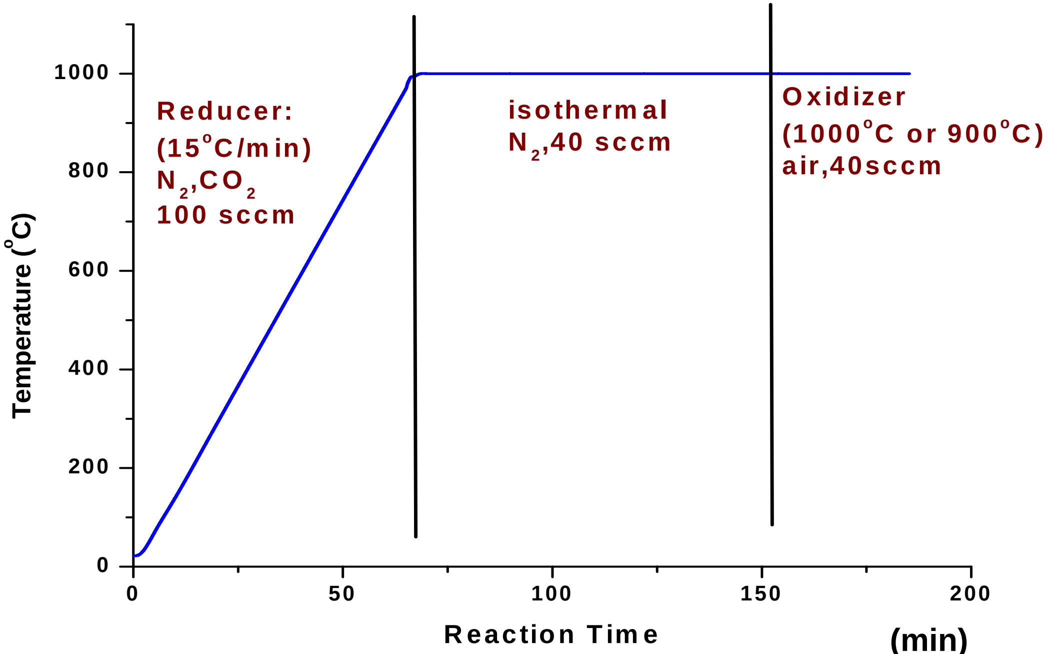


- Metal/metal oxide (Me/MeO) transfers oxygen to the fuel.
- Air is not mixed up with fuel
- CO_2 is not diluted with N_2 of flue gas
- Reduced NOx problems
- Sequestration ready CO_2
  - No additional energy penalty for the separation

Can solid fuels be used *directly* with chemical looping combustion?

Experimental Approach

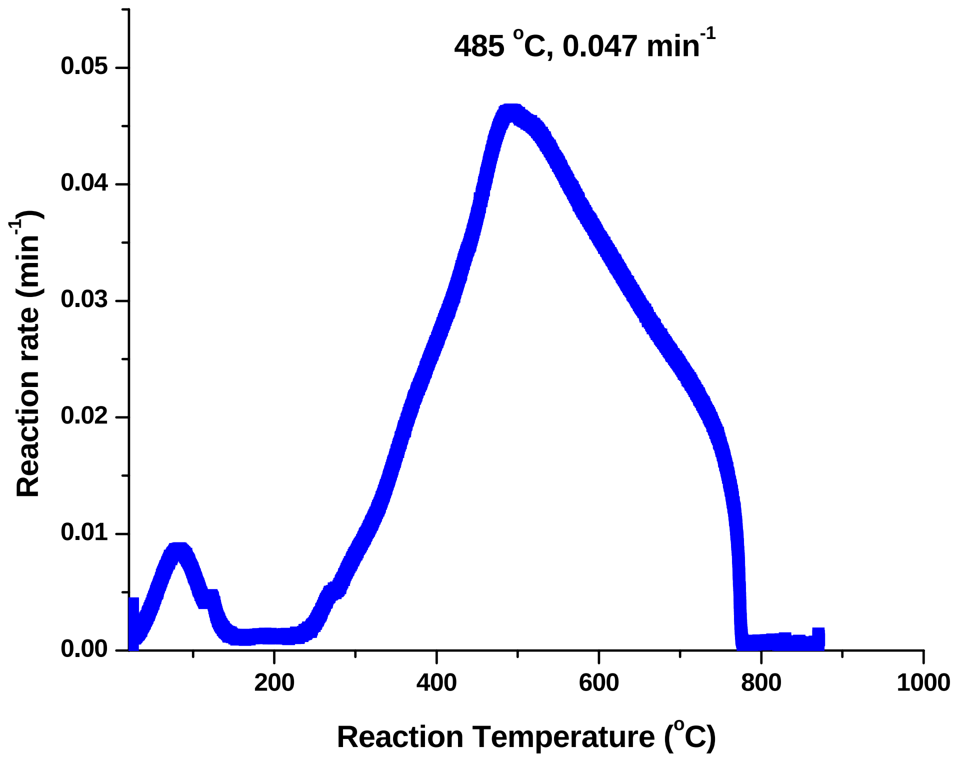
- **Mixture of coal with metal oxides (CuO, NiO, Fe_2O_3 Co_3O_4 and Mn_2O_3) or bentonite supported metal oxides weight ratio: 0.2 (coal) : 3-.5(MeOx)**
- **Gases in reducer: N_2, CO_2**
- **TGA temperature segments:**



TGA Combustion of Coal in Air

Coal Components
(Illinois #6,100 micron)

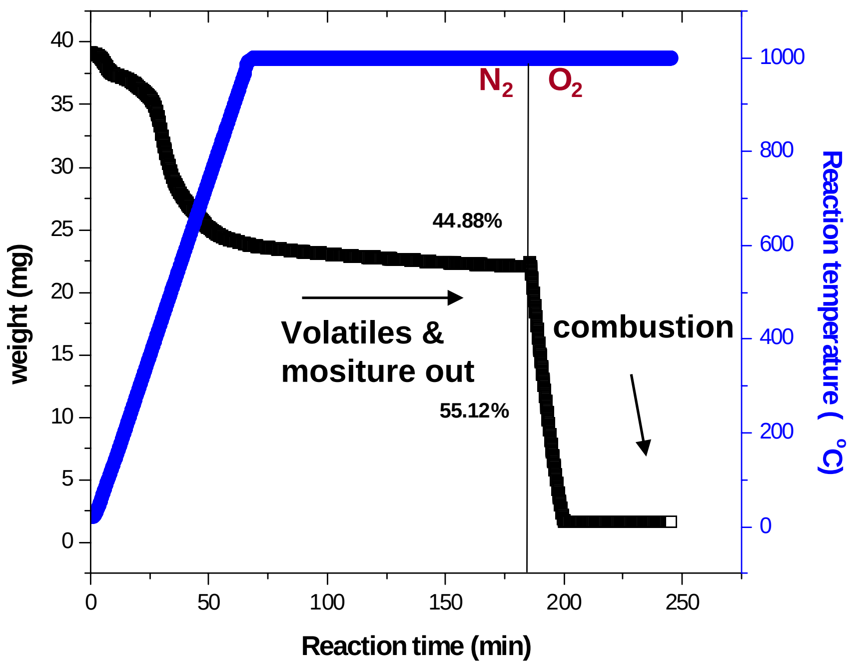
Contaminant	Concentration %
moisture	7.44
Volatiles	37.97
ash	12.45%
H	4.63
C	67.32
N	1.3
S	4.81
O	9.49



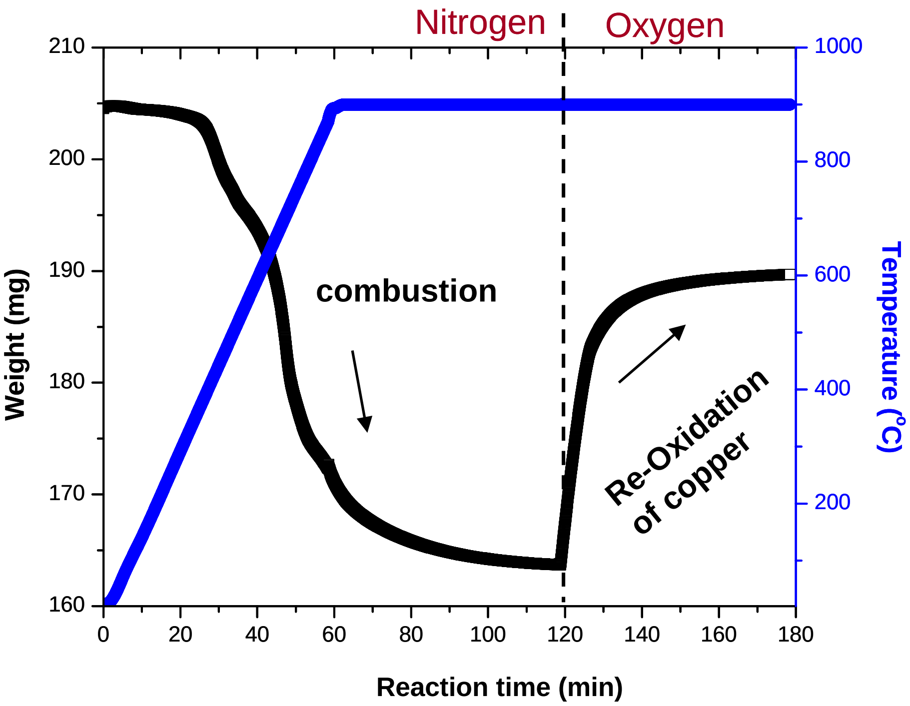
% comb. =100

Comparison of heating/combustion to chemical looping combustion

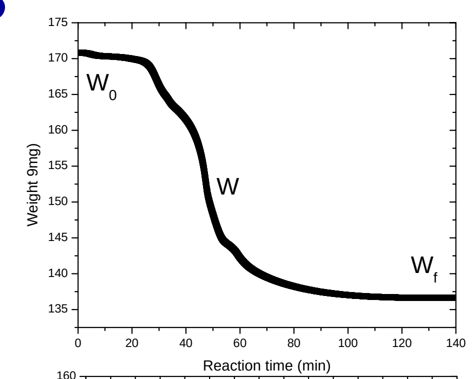
TGA Profile of Coal in N_2

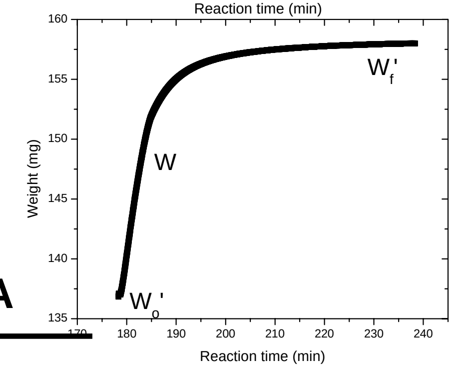


TGA Profile of Coal +CuO in N_2



Reaction Rate Calculations





- **Fractional Reduction (X) = $(W_o - W)/(W_o - W_f)$**
- **Fractional Oxidation (X) = $(W - W_o')/(W_f' - W_o')$**
- **Reaction rate=dX/dt**
- **% combustion=** $\frac{\text{Actual weight loss of coal from TGA}}{\text{Theoretically coal weight in sample}}$

Assuming carbon totally converted to CO_2, while in-line MS did not detect CO during combustion

- **Oxygen uptake (%)=** $\frac{\text{Experimental oxygen consumption}}{\text{Theoretical capacity for oxygen consumption}}$

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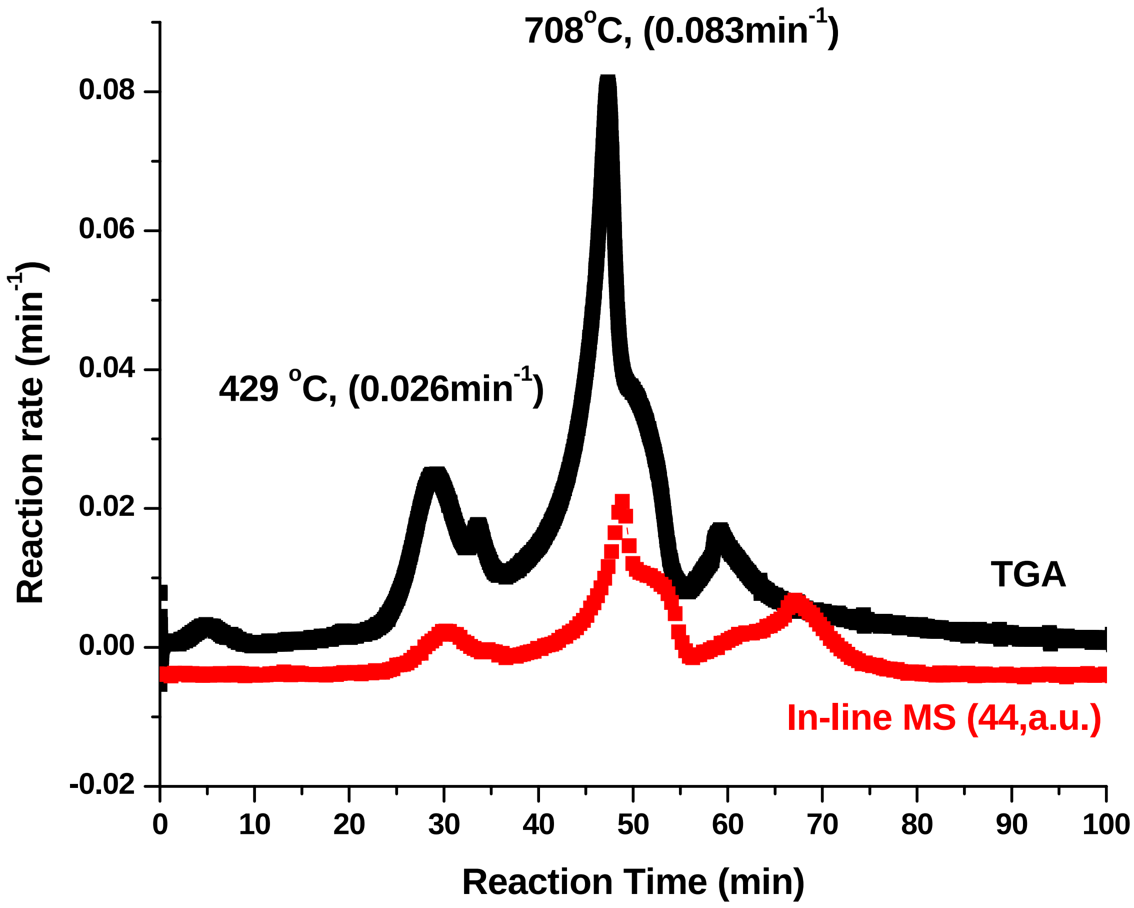
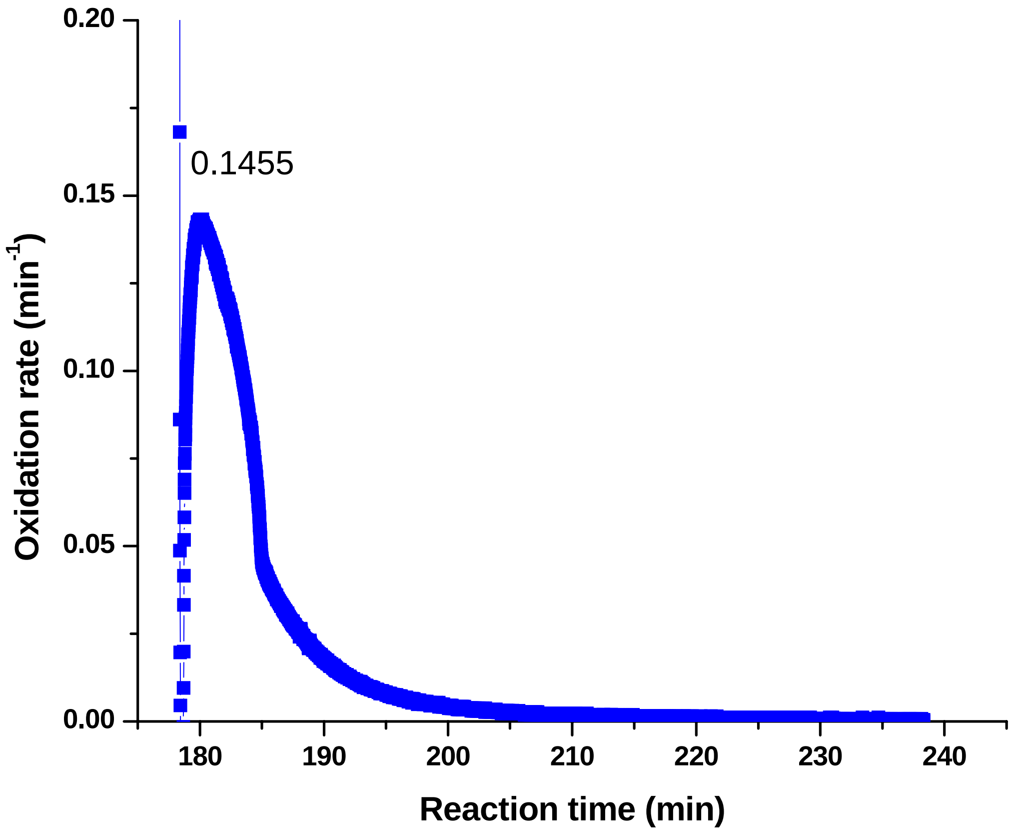
Reduction Segment of Coal+CuO in N_2



+major reaction happens at ~700 ºC, which is ideal for CLC process design
+CO2 combustion obtained from in-line MS matches TGA profiles
+In-line MS does NOT detect CO

Oxidation Segment of CuO in Air at 900 °C



Faster oxidation rates than combustion rates

Coal-CLC of Various Metal Oxides in CO_2

sample	Combustion				Oxidation		
	Comb. Temp.(°C)	Comb. Rate (min^{-1})	% combustion	ΔH (KJ/mol)	Oxi. Rate (min^{-1})	Oxygen uptake(%)	ΔH (KJ/mol)
CuO	703	0.098	100	-96.5	0.172	98.6	-156
Fe_2O_3	973	0.055	94.9	79.2	0.77	83.7Fe(II)	-347.4
NiO	993	0.061	73.05	75.2	0.84	77.5	-327.7
Mn_2O_3	905	0.011	76.76	-36.1	0.42	72.2Mn(II)	-216.4
Co_3O_4	781	0.096	83.3	-8.6	1.74	78.2 Co(II)	-243.9

CuO reacted at 900 °C, other metal oxides reacted at 1000 °C

Slight exothermic reaction for Mn_2O_3 and Co_3O_4 reduction
Endothermic reaction for NiO and Fe_2O_3 reduction

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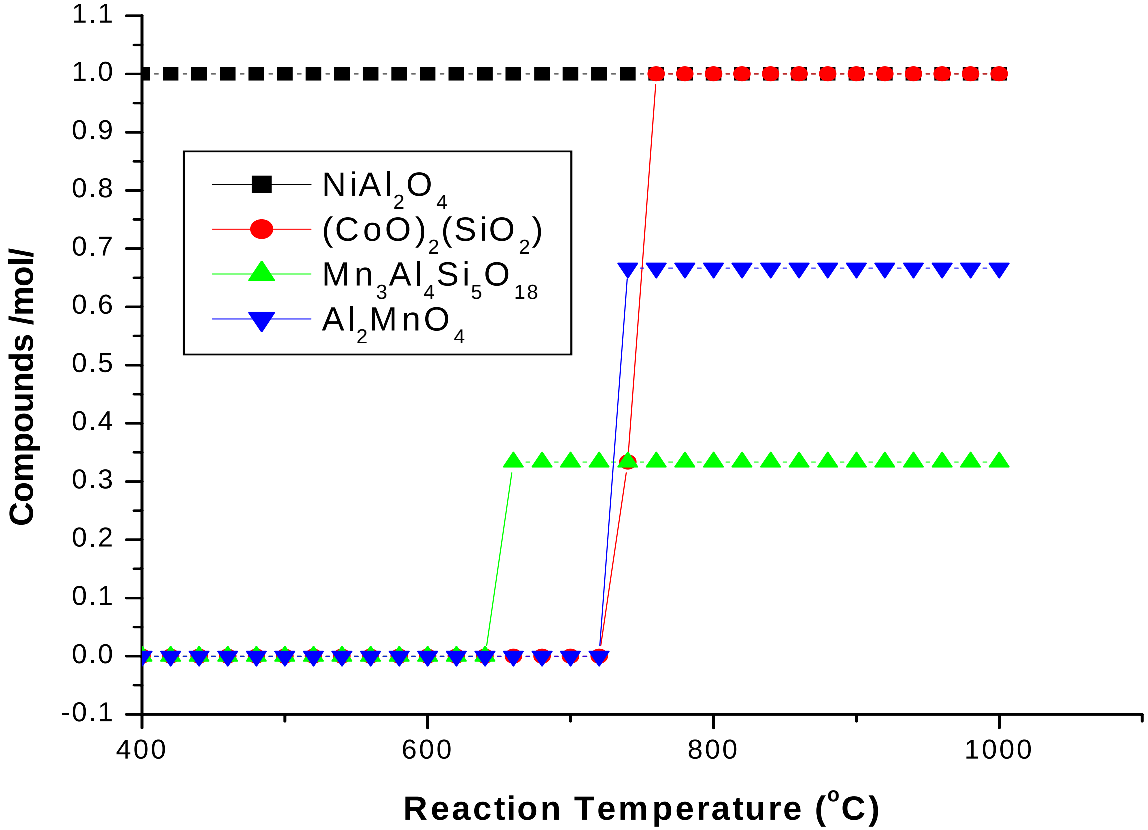
Thermodynamic (FactSage) Calculation on Metal Oxides and Ash

(Al_2O_3:SiO_2:MeO_x=1:1:1, Temp. up to 1000 °C)

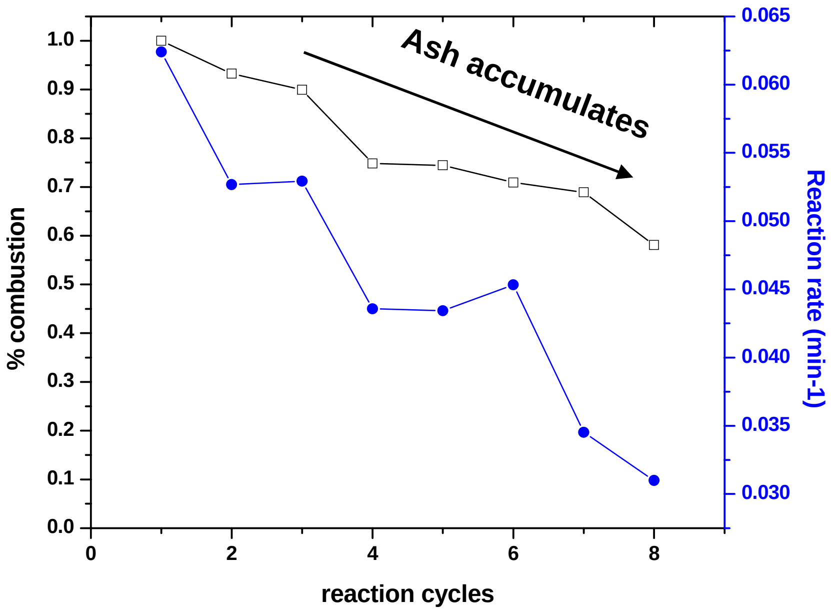


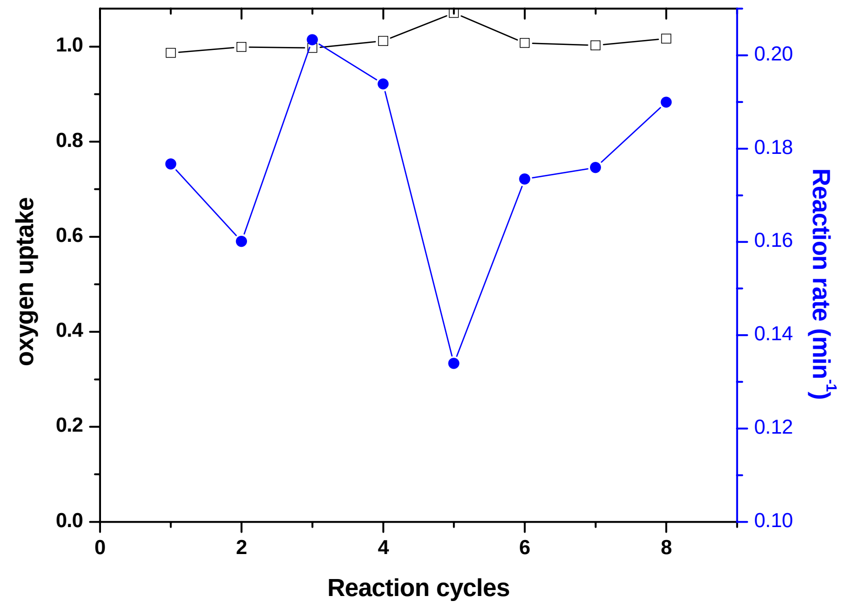
+strong interaction between ash and NiO, Co_3O_4 and Mn_2O_3

+Interaction between ash with CuO and Fe_2O_3 is NOT thermodynamically favorable

Multiple Cycle Test of CuO over Coal-CLC in N_2

(NO ash removal)





+CuO possess excellent combustion and oxidation performance in multiple cycle tests over coal-CLC
+ The combustion percentage and combustion rate decrease due to the accumulation of ash
+ Oxygen uptake and oxidation rate keep constant
+ Fair combustion and oxidation performance obtained in 8th cycle even without ash separation

Summary

- Combustion of coal feasible with metal oxides
  - +Metal oxides could supply oxygen for direct coal combustion
  - +Excellent combustion and re-oxidation performance in N2
  - + Produces sequestration ready-CO_2 by recycling CO_2 in reducer
- TGA and bench scale reactor tests proved that CuO possess excellent reduction/oxidation performance, and has a potential for an excellent oxygen carrier for solid-CLC.
- Carbon dioxide can also promote the combustion reaction for some metal oxides (results not presented here).
- The reduced metal could be easily re-oxided to metal oxide for looping reaction, the oxidation rate is faster than the reduction rate.