An Investigation of Bimetallic Cu-Fe and Mn-Fe Oxygen Carriers for Coal Chemical looping assisted by Oxygen Uncoupling (CLaOU)

Ping Wang, Nicholas Means, Bret Howard, Dushyant Shekhawat

Clean coal technologies 2019 conference

NATIONAL ENERGY TECHNOLOGY LABORATORY

Outline

- Briefly describe two direct coal chemical looping combustion (CLC): iG-CLC and CLOU
- Motivation for studying bimetallic oxygen carriers for coal chemical looping combustion
- Objectives
- Develop Cu-Fe and Mn-Fe oxygen carrier with an inert support of SiO_2 and ZrO_2 for high temperature coal CLC
- Summary

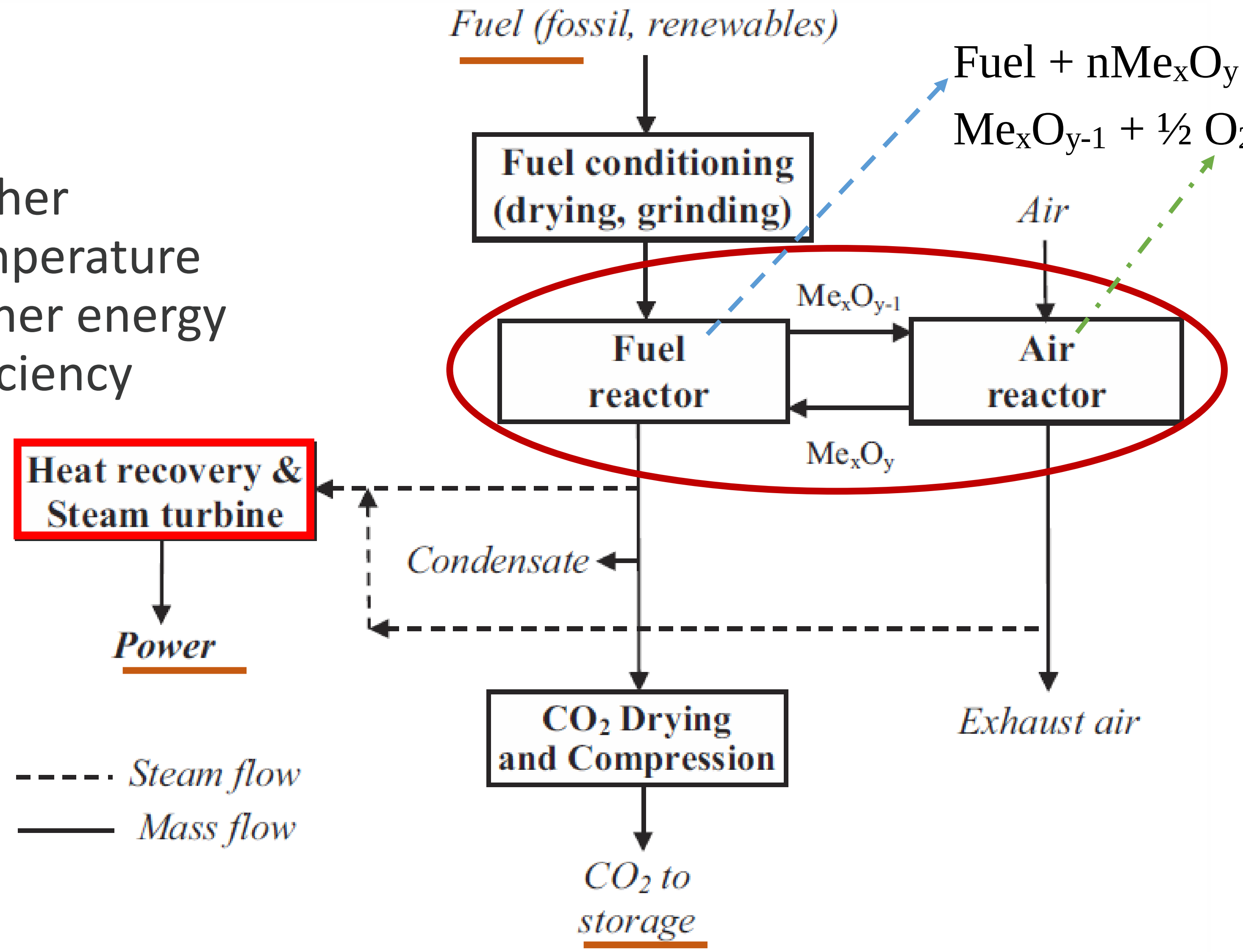
CLC Power Generation with Carbon Capture

NATIONAL ENERGY TECHNOLOGY LABORATORY

$$Fuel + nMe_xO_y \longrightarrow nMe_xO_{y-1} + H_2O + CO_2$$

$$Me_xO_{y-1} + ½ O_2 \longrightarrow Me_xO_y$$

Higher temperature higher energy efficiency



Calin-Cristian Cormos. Chemical looping with oxygen uncoupling (CLOU) concepts for high energy power generation with near total fuel decarbonization. Applied Thermal Engineering 112 (2017) 924-931

Progress in Oxygen Carrier Developments for Coal CLC

NATIONAL ENERGY TECHNOLOGY LABORATORY

Concept development and lab testing (1-1000kW$_{th}$)

- Important OC properties
  - High reactivity and oxygen transfer capacity
  - High attrition resistance

→

Scale-up and industrial validation

- Upscaling of OC manufacture
  - Produce at multi-ton scale and competitive price
  - Waste disposal, health and safety
- Upscaling reactor system
- Optimize the OC and the system for fuels

Gauthier, T.; Yazdanpanah, M.; Forret, A.; Amblard, B.; Lambert, A.; Bertholin, S. Clc, a promising concept with challenging development issues. *Powder Technology* **2017**, *316*, 3-17.

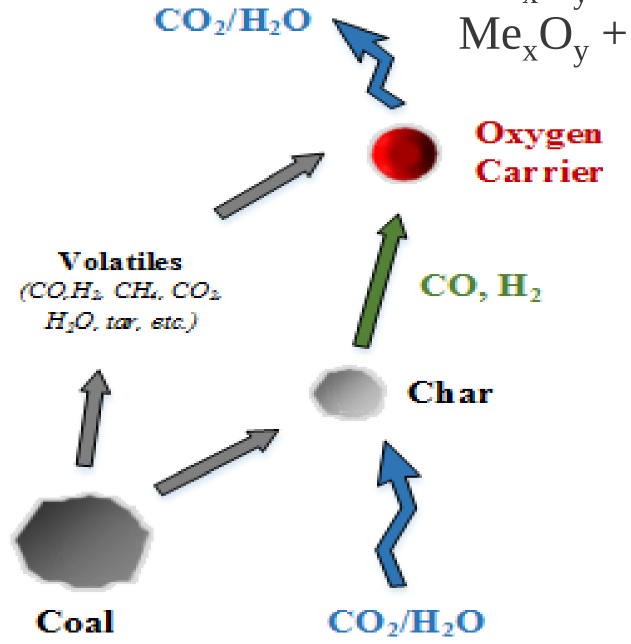
Main Reactions in Fuel Reactor for Direct Coal CLC

NATIONAL ENERGY TECHNOLOGY LABORATORY

IG-CLC (In-situ gasification chemical-looping combustion)

OC: Fe_2O_3, NiO, CuO

$$Me_xO_y + CO_{(g)} \longrightarrow CO_{2(g)} + Me_xO_{y-1}$$
$$Me_xO_y + H_{2(g)} \longrightarrow H_2O_{(g)} + Me_xO_{y-1}$$



Rate limiting step

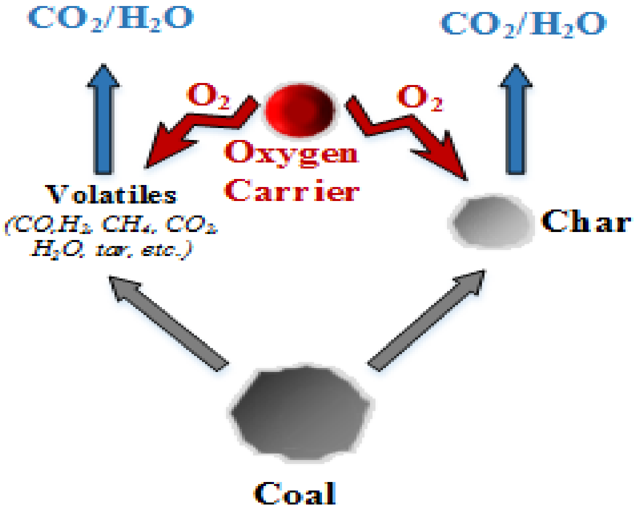
$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$
$$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)}$$

$$Coal \rightarrow volatiles + char\ (C)$$

CLOU (Chemical-looping with oxygen uncoupling)

OC: CuO, Mn_2O_3, Co_3O_4

$$2Me_xO_y \leftrightarrow 2Me_xO_{y-1} + O_{2(g)}$$
$$volatiles + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)}$$
$$char\ (C) + O_{2(g)} \rightarrow CO_{2(g)}$$



$$Coal \rightarrow volatiles + char\ (C)$$

Mn-Fe and Cu-Fe Oxygen Carriers for Coal CLaOU

NATIONAL ENERGY TECHNOLOGY LABORATORY

IG-CLC
OC: Fe_2O_3
Disadvantage:
- Slow reaction rate

CLOU
OC: CuO, Mn_2O_3
Disadvantage:
- Attrition problem

Chemical looping assisted by Oxygen Uncoupling (CLaOU)

Combined Mn-Fe and Cu-Fe OC advantages
- Enhance and improve the parent metal oxides

Objectives

Develop Cu-Fe and Mn-Fe oxygen carriers supported on SiO_2 and ZrO_2 with favorable reactivity at high operation temperature

- Study the reactivity and CO_2 conversion efficiencies of Cu-Fe and Mn-Fe OCs with coal char compared to monometallic Fe OC
- Discuss the main reactions taking place in CLaOU

Mn-Fe and Cu-Fe OC Preparations

- Pelletizing by pressure

  Paste, pellet, calcine at 1100°C, grind and sieve (<180μm)

- Mn-Fe and Cu-Fe compositions (wt.%)

	Mn_2O_3	CuO	Fe_2O_3	SiO_2	ZrO_2	Calcine at 1100°C
FeSi (reference)			60	40		√
MnFeSi	40		20	40		√
MnFeZr	40		20		40	√
CuFeSi		40	20	40		X
CuFeZr		40	20		40	√

Mn-Fe and Cu-Fe OC Characterizations

Mn-Fe and Cu-Fe OC Characterization	
Reactivity	Oxygen Uncoupling
	Reduction with **Coal Char**
	Multicycle CLaOU
BET	Surface Area and Porosity
XRD	Crystalline Phase Composition

Coal char preparation:

- Pyrolysis of Powder River Basin (PRB) sub-bituminous coal with particle size from 106 to 180 μm at 1100°C

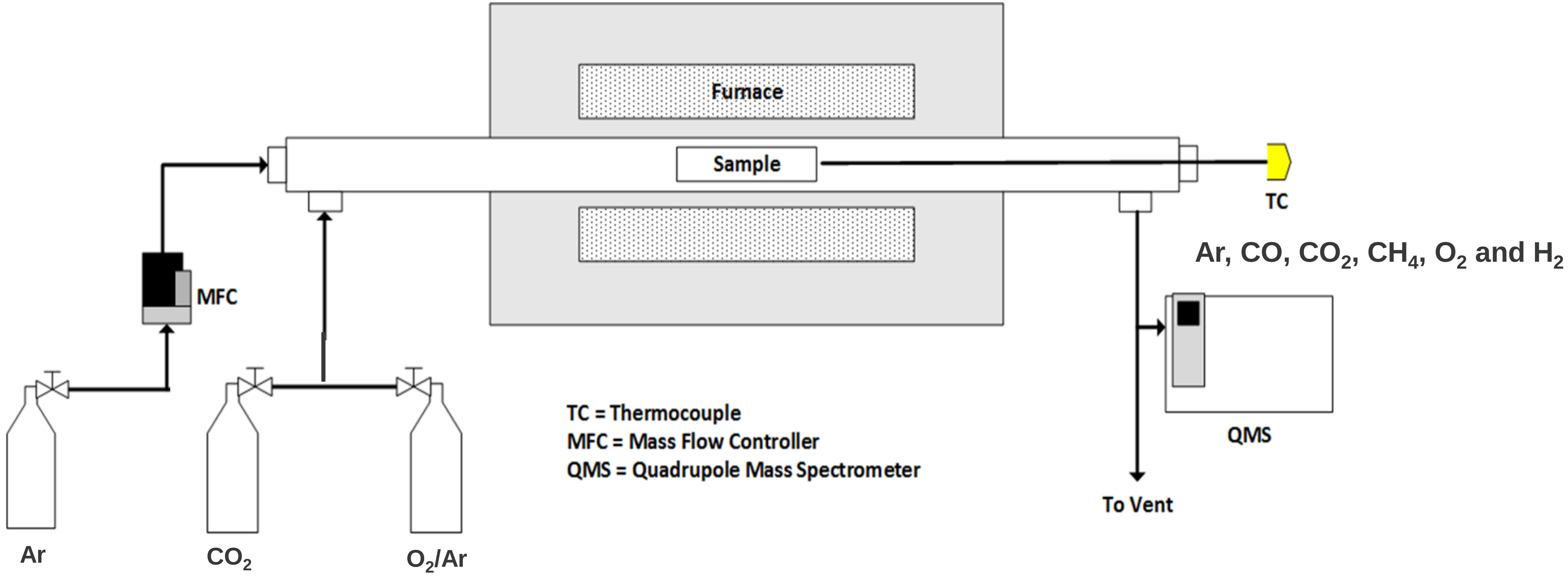
Coal char Property

Proximate analysis (% day basis)		
Volatile	**Fixed carbon**	**Ash**
3.02	**84.79**	**12.19**

Experimental Set-up and Test Conditions

NATIONAL ENERGY TECHNOLOGY LABORATORY

Fixed Bed Reactor- QMS System



Multicycle Test Conditions

- Reduction: Φ (OC/Char) = 70 and 50, 950 and 1050°C in ~10% CO_2/Ar
- Re-oxidization: 950 and 1050°C in ~10% O_2/Ar

Data Analysis

- **Oxygen uncoupling**

  Oxygen uncoupling Xo, $Xo = \frac{n_o}{n_{thero}}$

  Oxygen uncoupling rate, dXo/dt

- **Carbon conversion**

  Carbon conversion Xc, consider CO_2 and CO from combustion (full or partial), gasification, and reduction

  $$Xc = \frac{n_c}{n_0} = \frac{\sum_{t=0}^{t} F(yco_2+yco)}{n_0}$$

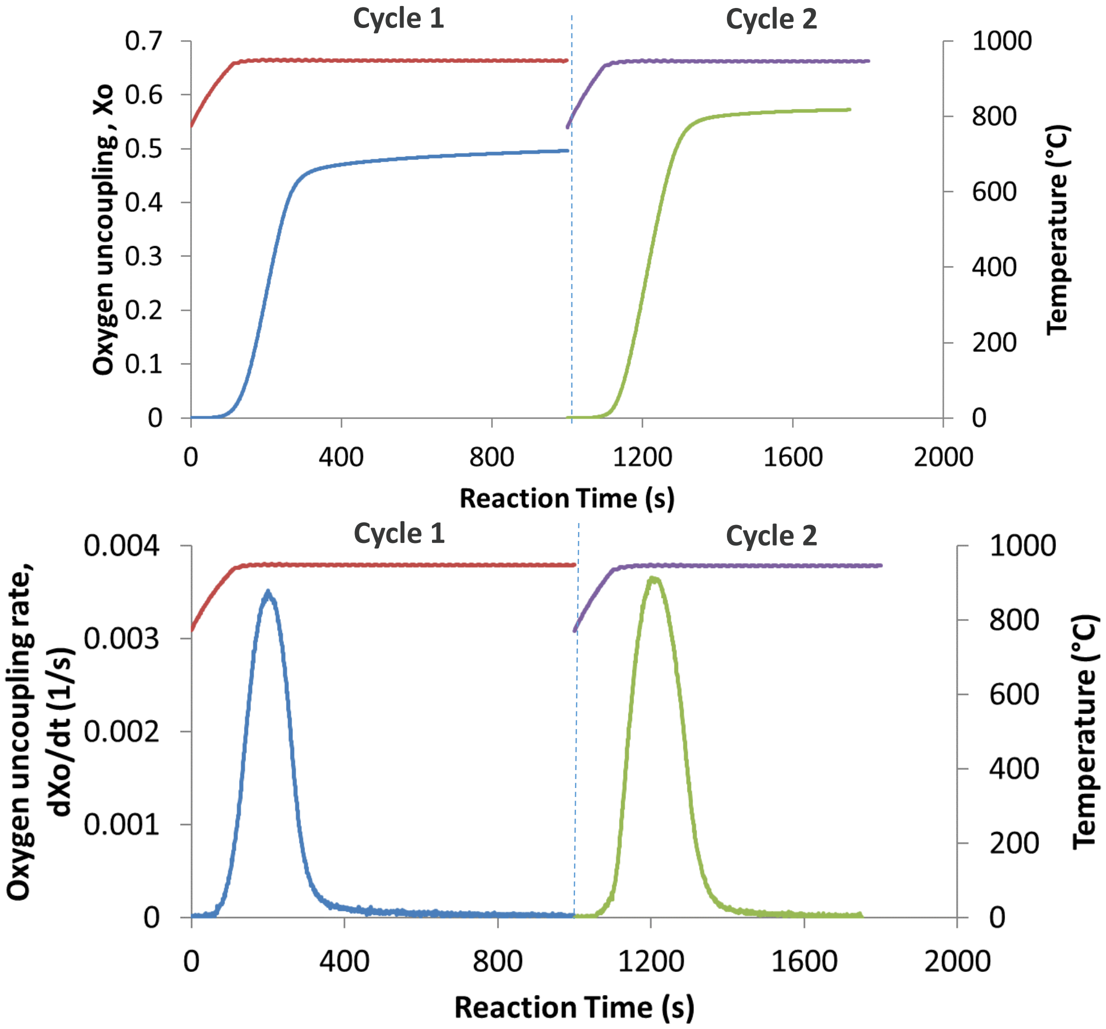
  Carbon conversion rate, dXc/dt

  CO conversion Xco, $Xco = \frac{n_{co}}{n_0} = \frac{\sum_{t=0}^{t} Fyco}{n_0}$

- **CO_2 conversion efficiency**

  $$Sco_2 = \frac{n_{co2}}{n_{co2}+n_{co}}$$

Oxygen Uncoupling of Mn-Fe and Cu-Fe OCs



CuFeZr oxygen uncoupling (Xo) and its rate (dXo/dt) at 950ºC in ~10% CO2/Ar

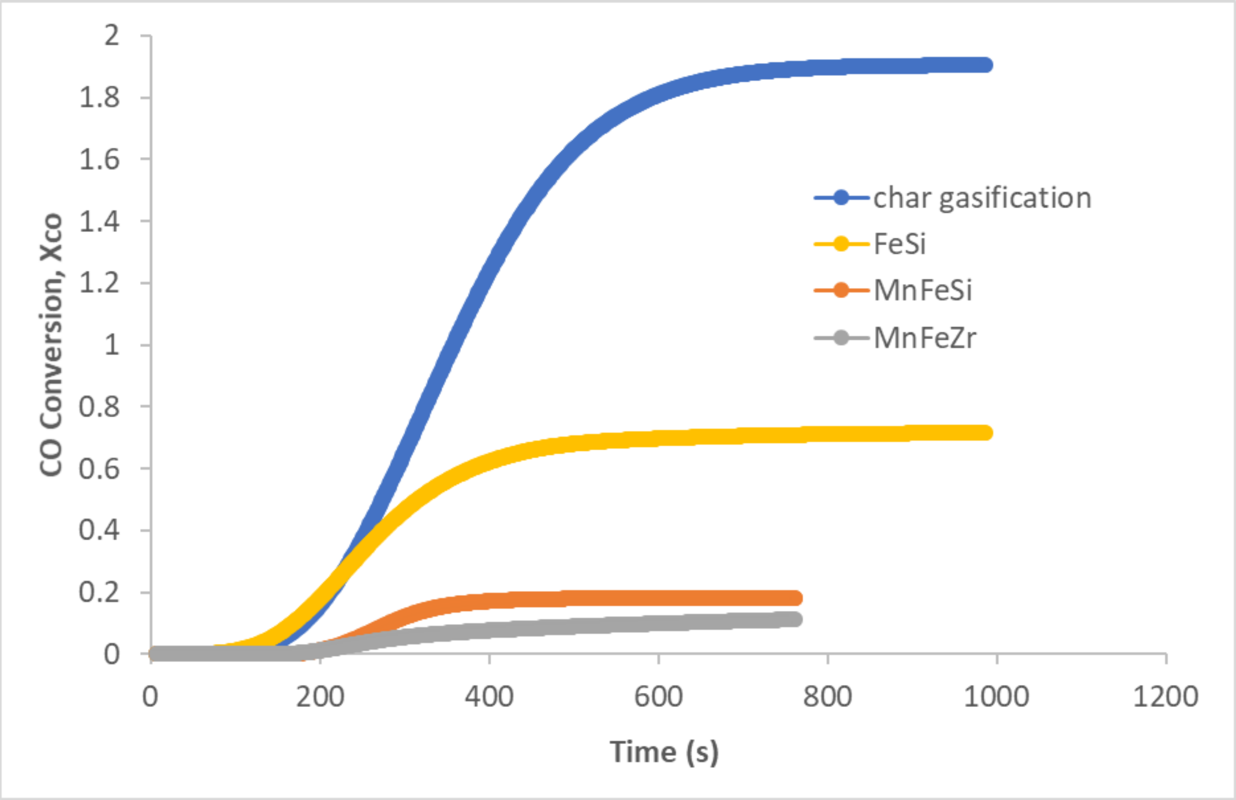
CuFeZr OC

- Higher oxygen uncoupling in cycle 2 (Xo_2 = 0.5) than in cycle 1 (Xo_2 = 0.57)

MnFeSi and MnFeZr OCs

- Only oxygen uncoupling in cycle 1 but lost oxygen uncoupling in cycle 2 (very low oxygen uncoupling)
- Higher oxygen uncoupling at 950ºC than at 1050ºC for MnFeZr OC

Mn-Fe OC Reductions with Char and Char Gasification



CO conversions in Mn-Fe OC reductions with coal char with ϕ=70 and char gasification at 1050°C in ~10% CO_2/Ar

Char gasification (char+SiO_2)

- Generate only CO, final Xco=1.9

$$C + CO_2 \rightarrow 2CO$$

FeSi OC reduction

- Generate mainly CO with CO_2, final Xco=0.7

MnFe OC (with Si and Zr) reduction

- Generate mainly CO_2 with CO, final Xco=0.18, MnFeSi; Xco=0.12, MnFeZr

Multicycle tests-Si and Zr support of Mn-Fe OC

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Multicycle tests with ϕ=70 at 1050°C
- Mn-Fe OC improved reactivity with coal and CO_2 conversion efficiency compared to Fe OC
- MnFeZr OC has higher carbon conversion rate and CO_2 conversion efficiency than MnFeSi OC

Oxygen Carrier		Carbon conversion, Xc	Carbon conversion rate, dXc/dt (1/s)	CO_2 conversion efficiency, S_{CO_2}	Surface Characterization		
					BET Surface Area (m^2/g)	Pore Volume (cc/g)	Average Pore Diameter (Å)
FeSi	Cycle 1	0.77	0.0048	0	0.68	0.0064	375
	Cycle 2	0.81	0.0043	-0.17	0.32	0.0016	197
MnFeSi	Cycle 1	0.91	0.006	0.77	1.82	0.0076	167
	Cycle 2	0.89	0.006	0.48	0.7	0.0023	133
MnFeZr	Cycle 1	0.82	0.0082	0.87	0.9	0.0097	430
	Cycle 2	1.	0.0075	0.81	0.67	0.0064	197

Main Reactions in Mn-Fe OC Reductions with Char

FeSi OC

Gasification $C + CO_2 \rightarrow 2CO$

Reduction $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

MnFe OC (with Si and Zr)

Oxygen uncoupling $6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$

$$6(Mn_xFe_{1-x})_2O_3 \rightarrow 4(Mn_xFe_{1-x})_3O_4 + O_2$$

$$\frac{2}{3}Mn_7SiO_{12} + 4SiO_2 \rightarrow \frac{14}{3}MnSiO_3 + O_2$$

Combustion $C + O_2 \rightarrow CO_2$

$$2CO + O_2 \rightarrow 2CO_2$$

Gasification $C + CO_2 \rightarrow 2CO$

Reduction $M_xO_y + CO \rightarrow M_xO_{y-1} + CO_2$

$$Mn_3O_4 + CO \rightarrow 3MnO + CO_2$$

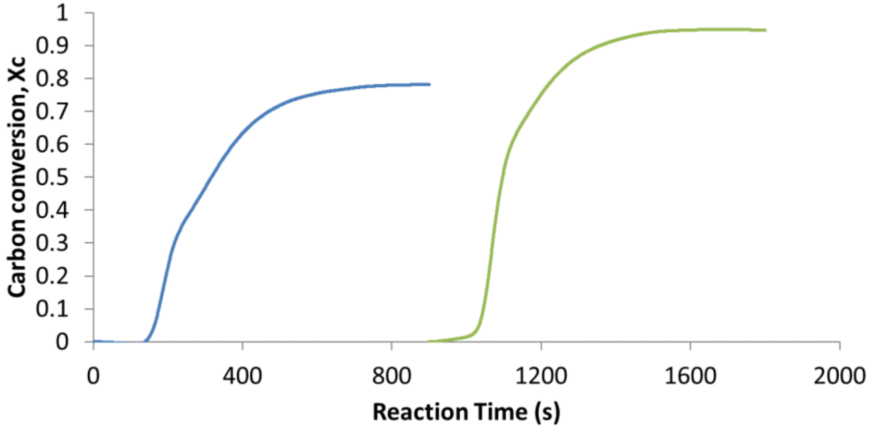
OC	XRD phase analysis		
	Fresh	Reduced	Used
FeSi	Fe_2O_3	Fe_3O_4 Fe_2SiO_4	Fe_2O_3
MnFeSi	Mn_2O_3 Mn_7SiO_{12}	$Mn_{1.03}Fe_{1.97}O_4$ $Mn_{0.802}Fe_{0.198}O$ Mn_2SiO_4	$MnFe_2O_4$ $MnSiO_3$
MnFeZr	Mn_2O_3, $(Mn,Fe)_2O_3$	$Mn_{1.03}Fe_{1.97}O_4$ $Mn_{0.802}Fe_{0.198}O$ MnO	$Mn_{1.58}Fe_{1.42}O_4$

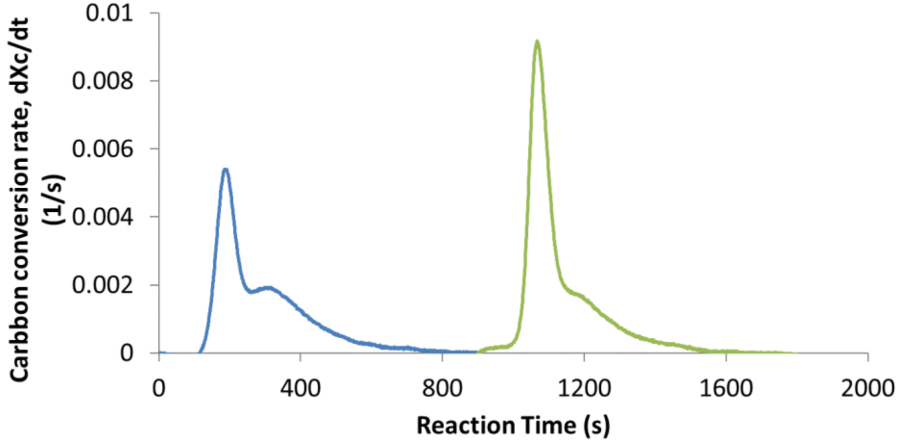
Multicycle tests-Cu-Fe and Mn-Fe OCs

NATIONAL ENERGY TECHNOLOGY LABORATORY

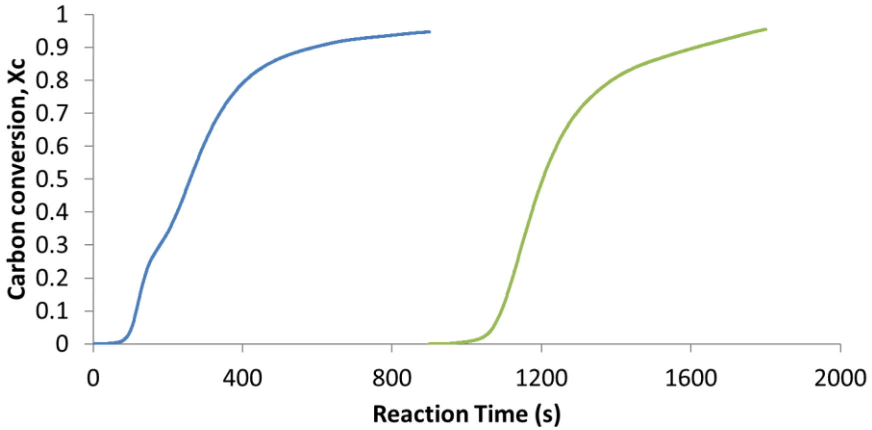
- Multicycle tests with ϕ=50 at 950^{o}C
- CuFeZr OC has higher carbon conversion rate than MnFeZr OC

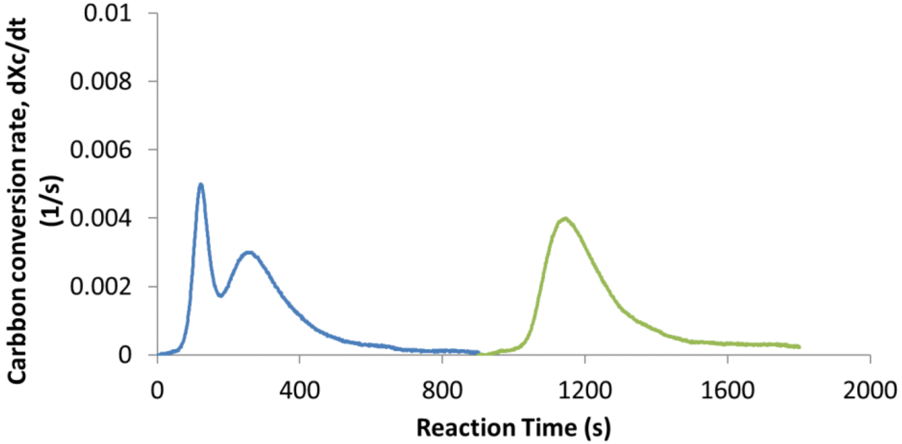
CuFeZr





MnFeZr





Multicycle tests-Cu-Fe and Mn-Fe OCs Main Reactions

NATIONAL ENERGY TECHNOLOGY LABORATORY

CuFeZr OC

Oxygen uncoupling $4CuO \rightarrow 2Cu_2O + O_2$ $4\,CuFe_2O_4 \rightarrow O_2 + 4\,CuFeO_2 + 2\,Fe_2O_3$

Combustion $C + O_2 \rightarrow CO_2$ $2CO + O_2 \rightarrow 2CO_2$

Gasification $C + CO_2 \rightarrow 2CO$

Reduction $Cu_2O + CO \rightarrow 2Cu + CO_2$ $CuFeO_2 + CO \rightarrow Cu + Cu_xFe_{3-x}O_4$ (X=0.67 or 0.86) $+ CO_2$

Oxygen Carrier		CO_2 conversion efficiency	Surface Characterization			XRD Phase Analysis		
			BET Surface Area (m^2/g)	Pore Volume (cc/g)	Average Pore Diameter (Å)	Fresh	Reduced	Used
MnFeZr	Cycle 1	0.89	0.9	0.0097	430	Mn_2O_3, $(MnFe)_2O_3$	$Mn_{1.03}Fe_{1.97}O_4$ $Mn_{0.802}Fe_{0.198}O$ MnO	$Mn_{1.58}Fe_{1.42}O$
	Cycle 2	0.64	0.46	0.006	518			
CuFeZr	Cycle 1	0.86	0.23	0.0023	397	CuO $CuFe_2O_4$	$CuFeO_2$ $Cu_xFe_{3-x}O_4$ Cu, Cu_2O	$CuFe_2O_4$ CuO
	Cycle 2	0.97	0.0687	0.00083	482			

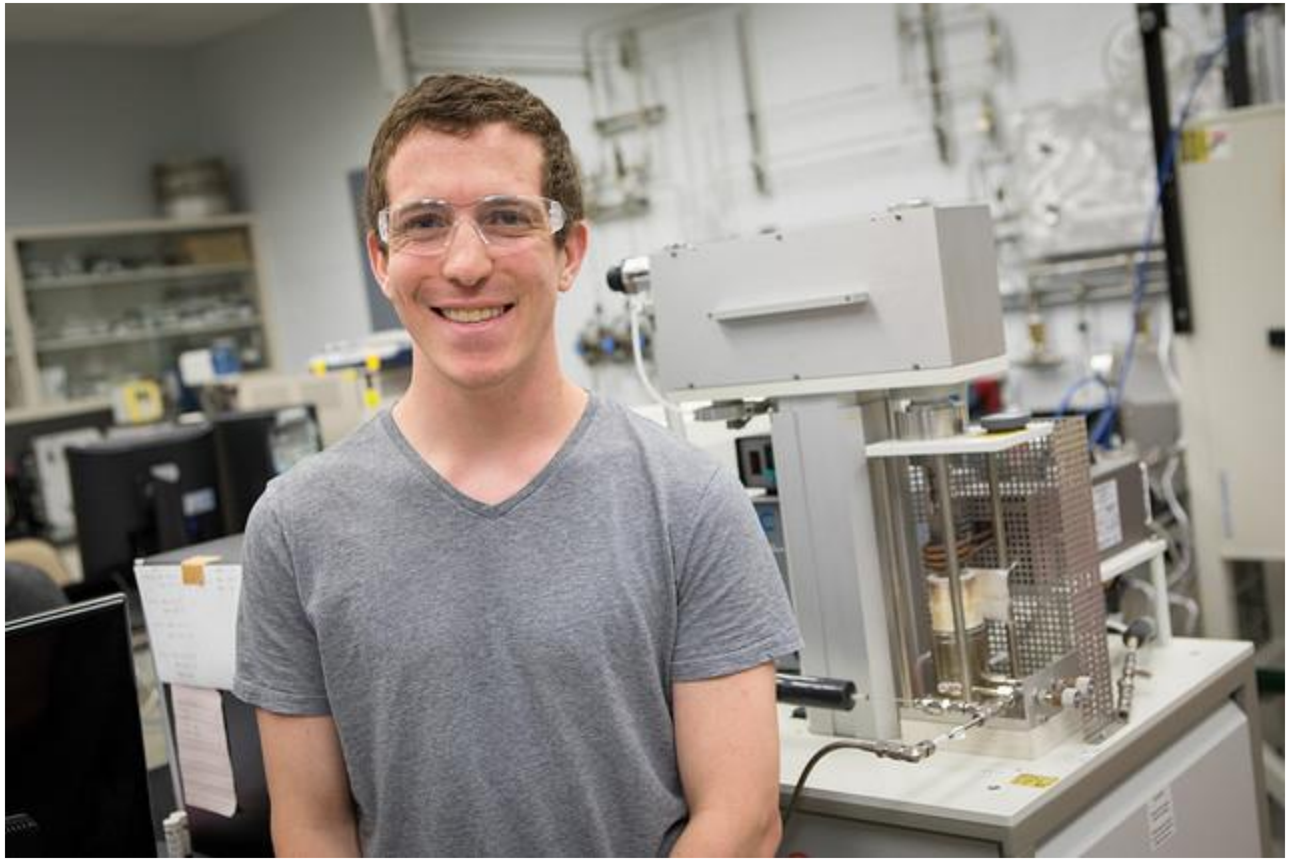
Summary

- Bimetallic Mn-Fe and Cu-Fe OCs demonstrated various degrees of oxygen uncoupling. Improved reactivity with coal char and better CO_2 conversion efficiency compared to monometallic Fe oxide without oxygen uncoupling capability was observed.
- MnFeZr OC has higher carbon conversion rate and CO_2 conversion efficiency than MnFeSi OC
- Cu-Fe OC at low φ had a higher reactivity compared to the Mn-Fe OC with same weight composition and conditions but Cu-Fe further reduced to Cu that potentially causes agglomeration at high temperature in the gasification environment.

Acknowledgements

DOE-Mickey Leland Energy Fellow

Tyler Weinstein



Thank You

Questions?