Development of Bimetallic Cu-Fe Oxygen Carriers for Coal Chemical-Looping Combustion

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NATIONAL ENERGY TECHNOLOGY LABORATORY

CLC Power Generation with Carbon Capture

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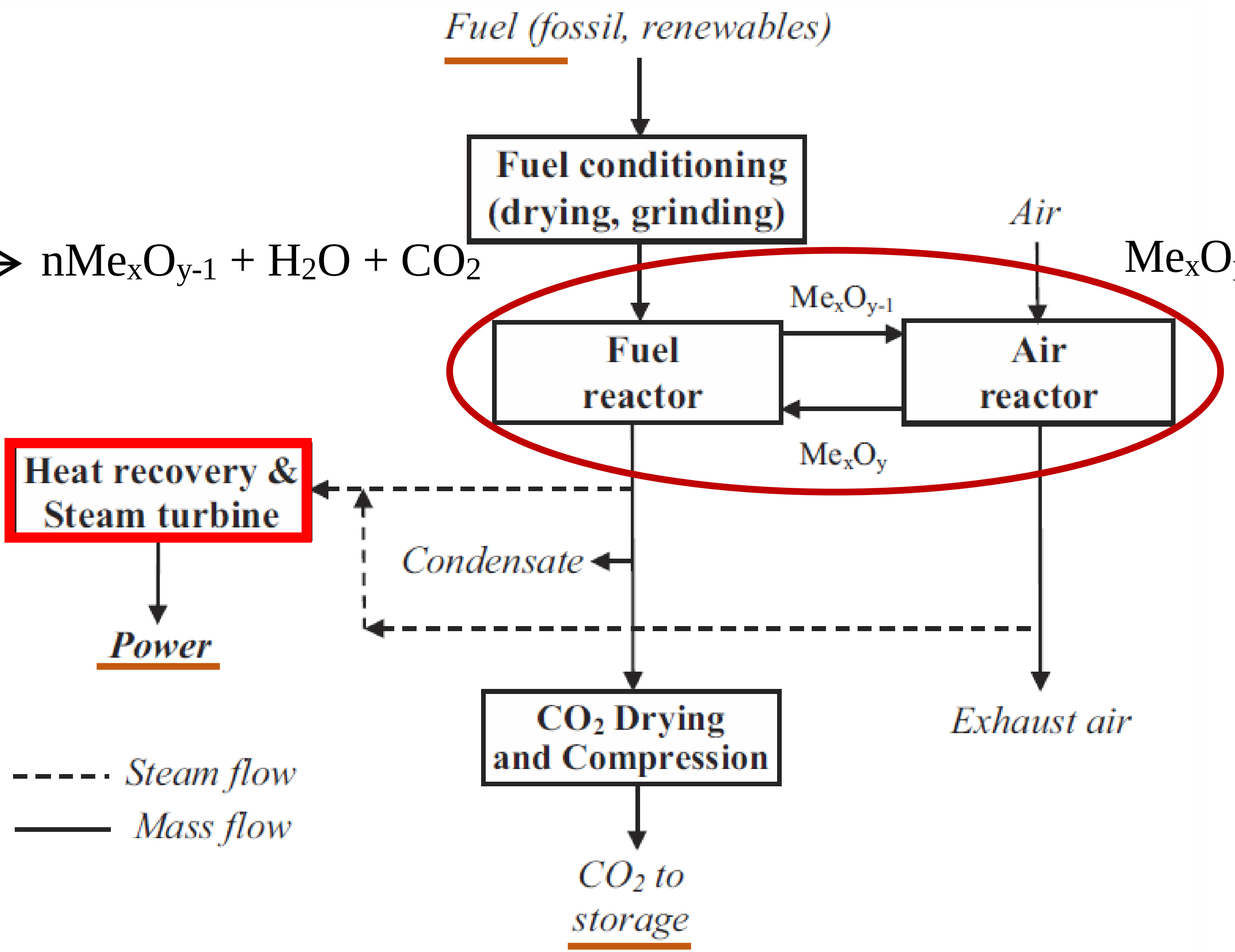
$Fuel + nMe_xO_y \longrightarrow nMe_xO_{y-1} + H_2O + CO_2$

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

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

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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

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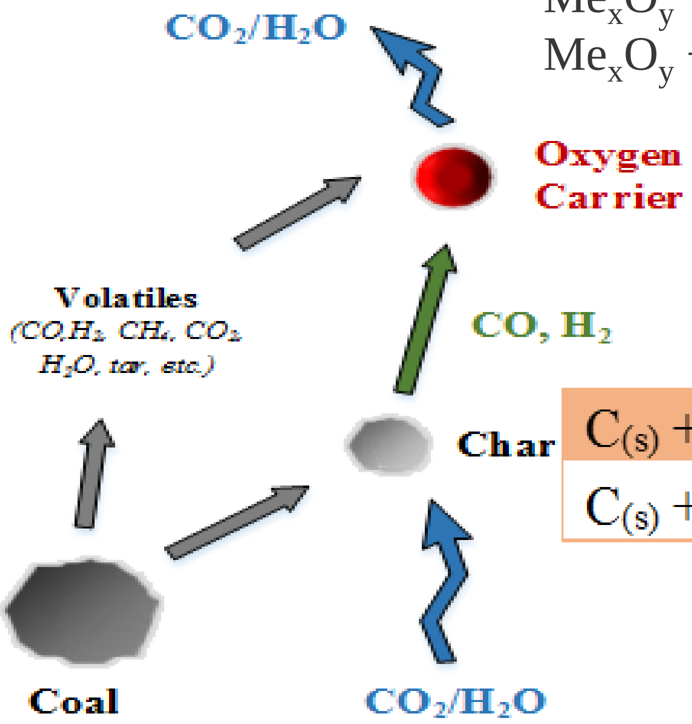
IG-CLC (In-situ gasification chemical-looping combustion)

OC: Fe_2O_3, NiO, CuO

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



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

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

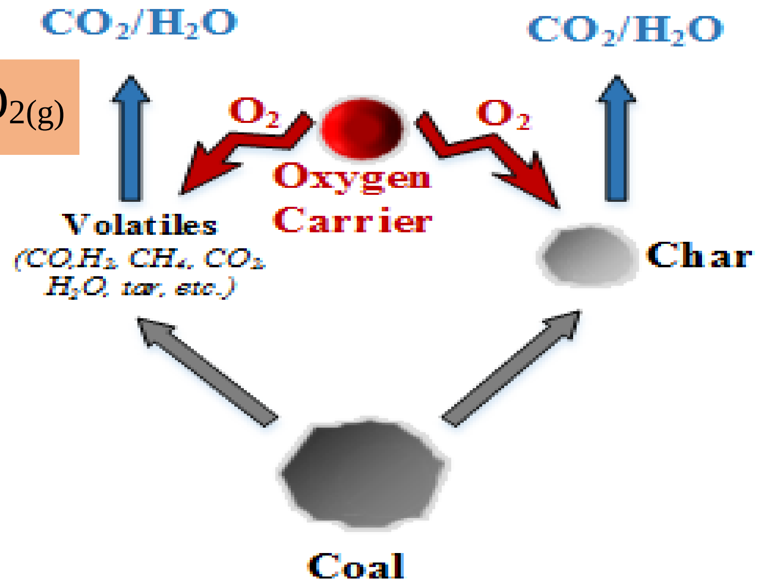
Rate limiting step

CLOU (Chemical-looping with oxygen uncoupling)

OC: CuO, Mn_2O_3, Co_3O_4

$$volatiles + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)}$$
$$char\ (C) + O_{2(g)} \rightarrow CO_{2(g)}$$

$$2Me_xO_y \leftrightarrow 2Me_xO_{y-1} + O_{2(g)}$$



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

U.S. DEPARTMENT OF ENERGY

Wang, P.; Means, N.; Shekhawat, D.; Berry, D.; Massoudi, M., Chemical-Looping Combustion and Gasification of Coals and Oxygen Carrier Development: A Brief Review. Energies 2015, 8 (10), 10605-10635.

Cu-Fe Oxygen Carriers for Coal IG-CLC and CLOU

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IG-CLC

OC: Fe_2O_3

Disadvantage:

- Low oxygen transport capability

  Fe_2O_3-Fe_3O_4-FeO-Fe

  Fe_2O_3/Fe_3O_4:0.033

  CuO/Cu_2O:0.1

CLOU

OC: CuO

Disadvantage:

- Mechanical stability

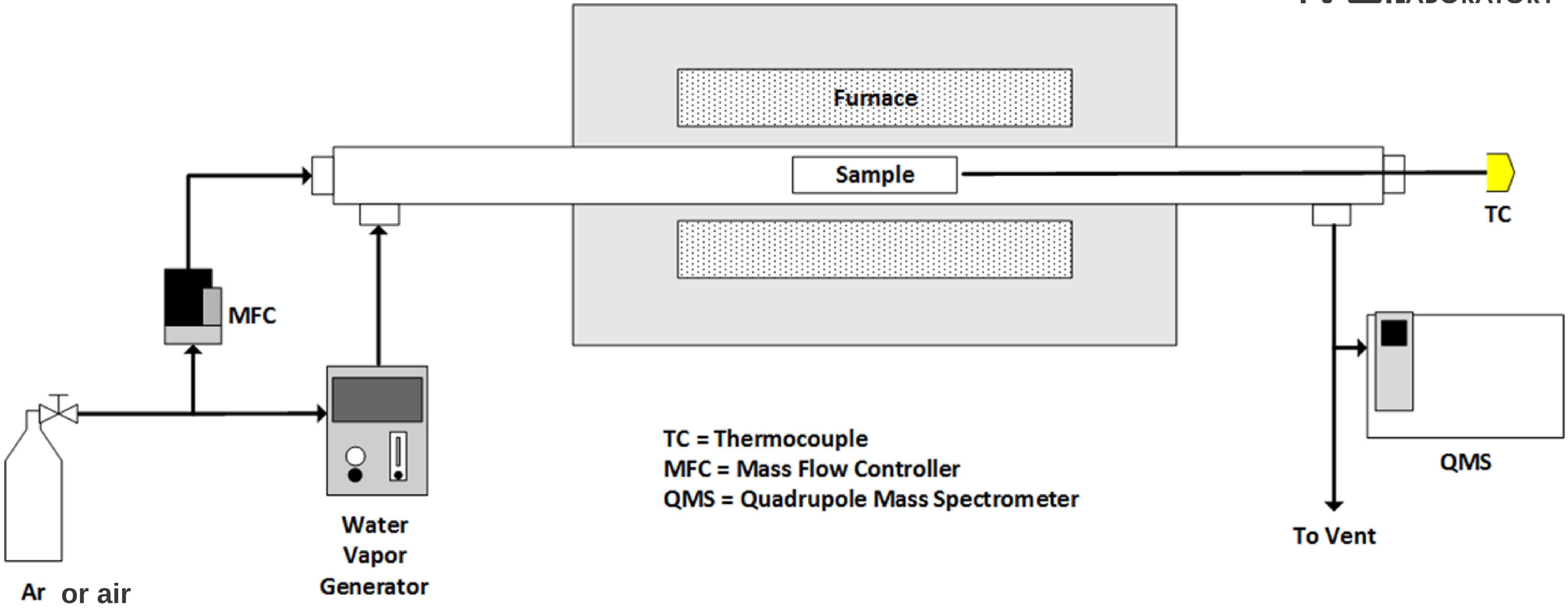
Combined Cu-Fe OC

- Keep the parent metal oxide advantages and overcome the parent metal oxide disadvantages
- Cu-Fe-Si is attractive based on its availability from naturally occurring materials with low cost

Objectives

- To prepare Cu-Fe-Si OC for iG-CLC and CLOU
- To study reactivity and CO_2 capture efficiencies of Cu-Fe-Si OC with coal char at high temperature (up to 1100°C) in iG-CLC and CLOU at different ratios of OC to coal char (by weight φ)
- To discuss main reactions taking place in iG-CLC and CLOU

Experiment Set-up



On-line quantitative measurement of the product gas constituents: Ar, CO, CO_2, CH_4, and H_2

X-ray diffraction (XRD) analysis of the phase composition of fresh OC and reacted OC

Data Analysis

- **Oxygen uncoupling**

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

  Oxygen uncoupling rate R, R=dXo/dt

- **Carbon conversion**

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

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

  Carbon conversion rate R, R=dXc/dt

- **CO_2 capture efficiency**

  $$\eta co_2 = \frac{n_{co2}}{n_0}$$

Coal and Char Properties

Coal char: pyrolysis of PRB sub-bituminous coal with particle size from 106 to 180 μm at 1000°C

	Proximate analysis (% day basis)		
	Volatile	Fixed carbon	Ash
Powder River Basin (PRB) Sub-bituminous coal char	1.98	85.6	12.42
PRB coal	45.08	47.66	7.26

	Ultimate analysis (% dry basis)				
	C	H	N	S	O (diff)
PRB coal	67.24	4.23	1.53	0.38	17.79

	Ash mineral analysis (oxides and ignited % wt.)									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	P_2O_5	MgO	Na_2O	K_2O	SO_3
PRB	38.71	16.00	5.52	1.08	19.24	0.96	4.68	1.22	0.75	10.69

Bimetallic Cu-Fe-Si OC Preparation

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- Pelletizing by pressure

  Paste, pellet, calcine at 1000 and 1100°C, grind and sieve (<180µm)

- IG-CLC

  Fe40 OC: 40%Fe_2O_3+20%CuO+40%SiO_2 by weight

  Fe40 OC phase mainly $CuFe_2O_4$ and SiO_2

  $CuO (s) + Fe_2O_3 (s) \rightarrow CuFe_2O_4 (CuOFe_2O_3)(s)$

- CLOU

  Cu40 OC: 40%CuO+20%Fe_2O_3+40%SiO_2 by weight

  Cu40 OC phase mainly CuO, $CuFe_2O_4$ and SiO_2

CuO wt.%	Calcination temp. (°C)	
	1000	1100
20	v	v
40	v	x
50	x	x
60	x	x

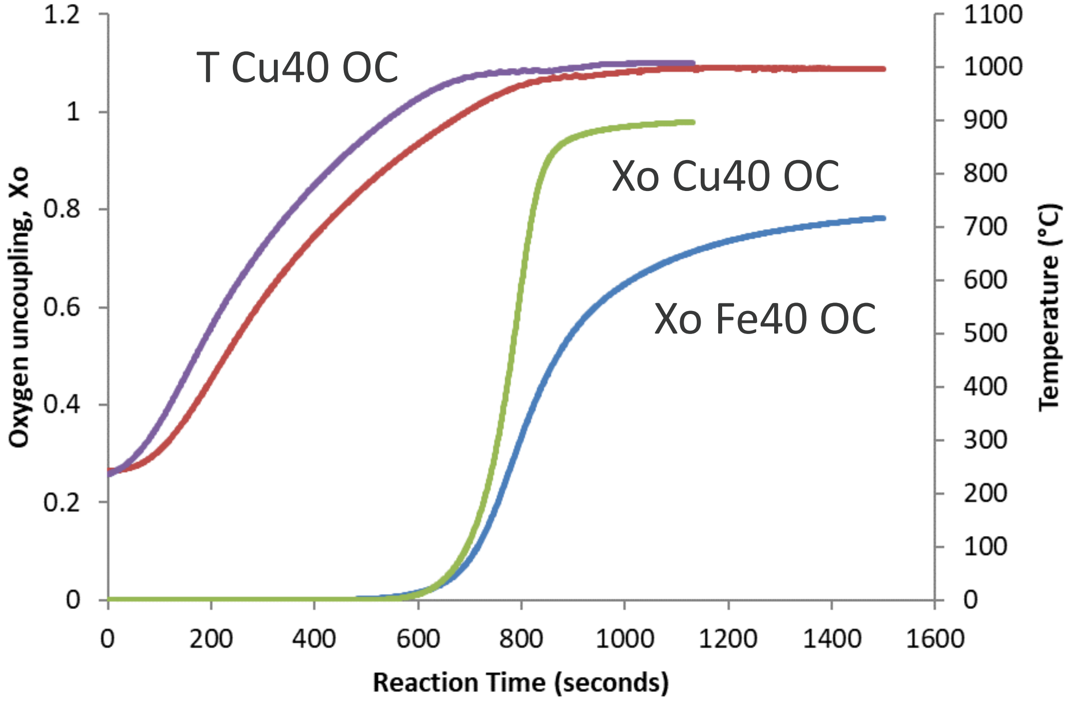
Oxygen Uncoupling of Fe40 OC and Cu40 OC

- Test in Ar at 1000°C
- Oxygen uncoupling(CuO to Cu_2O) Xo

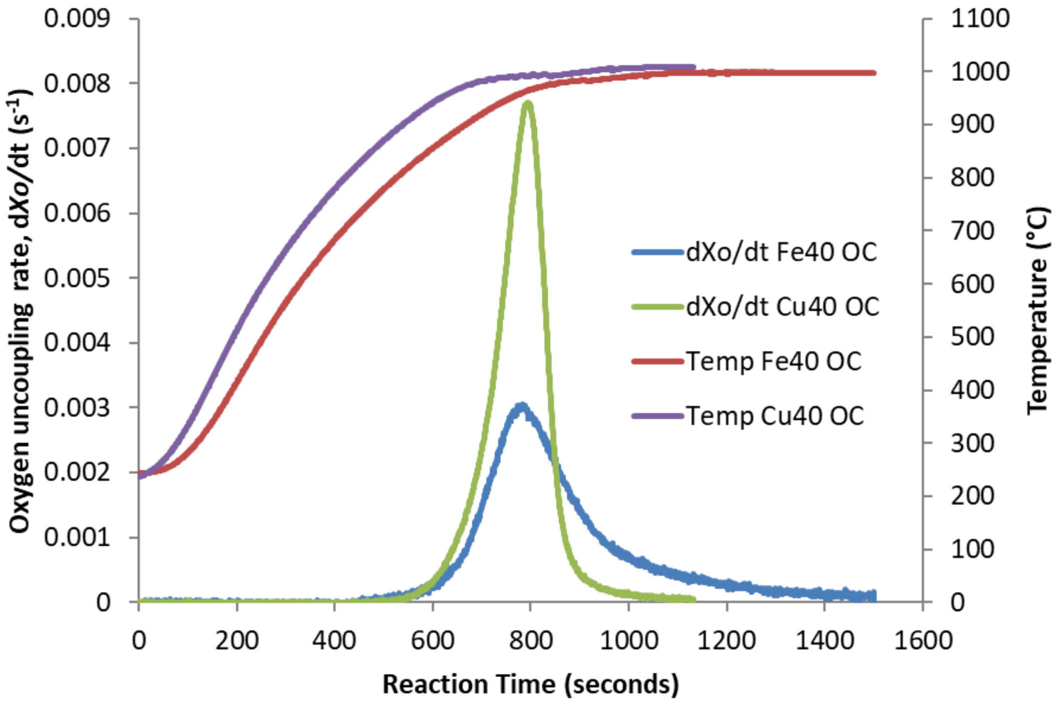
Fe40 OC: maximum Xo=0.78, dXo/dt=0.003 s^{-1}, Tmax=960°C

Cu40 OC: maximum Xo=0.98, dXo/dt=0.008 s^{-1}, Tmax=975°C

Fe 40 OC mainly phase change:
$CuFe_2O_4$ /$CuFeO_2$ ($Cu_2OFe_2O_3$)
Cu 40 OC mainly phase change:
CuO/Cu_2O, $CuFe_2O_4$/$CuFeO_2$



Fe40 OC and Cu40 OC oxygen uncoupling (Xo)

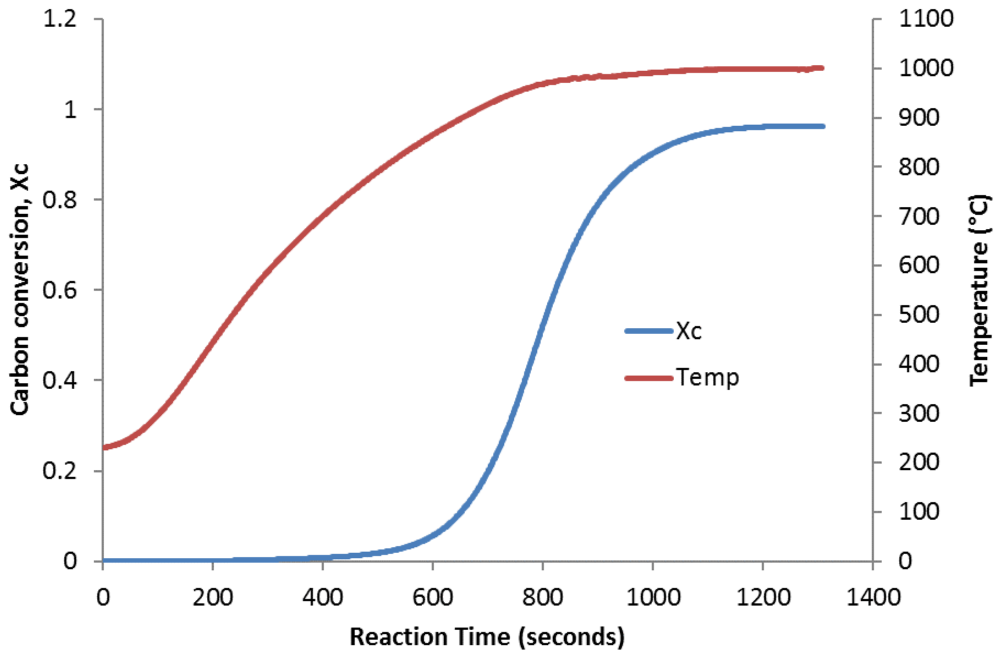


Fe40 OC and Cu40 OC oxygen uncoupling rate (dXo/dt)

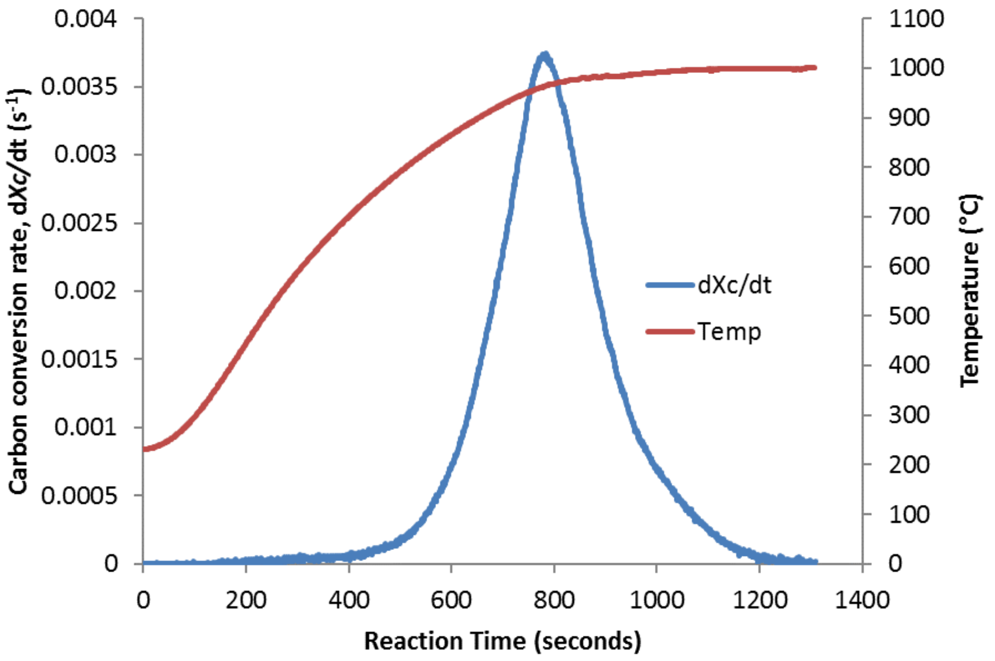
Fe40 OC with Coal Char in IG-CLC

Reactivity of Fe40 OC and char with φ 80 at 1000°C

- Select φ=80 considering CuO/Cu_2O and Fe_2O_3/Fe_3O_4
- Xc= 0.96, Theoretical Xc= 1
- Maximum dXc/dt=0.0037 s^{-1} at Tmax=956°C



Carbon conversion efficiency Xc

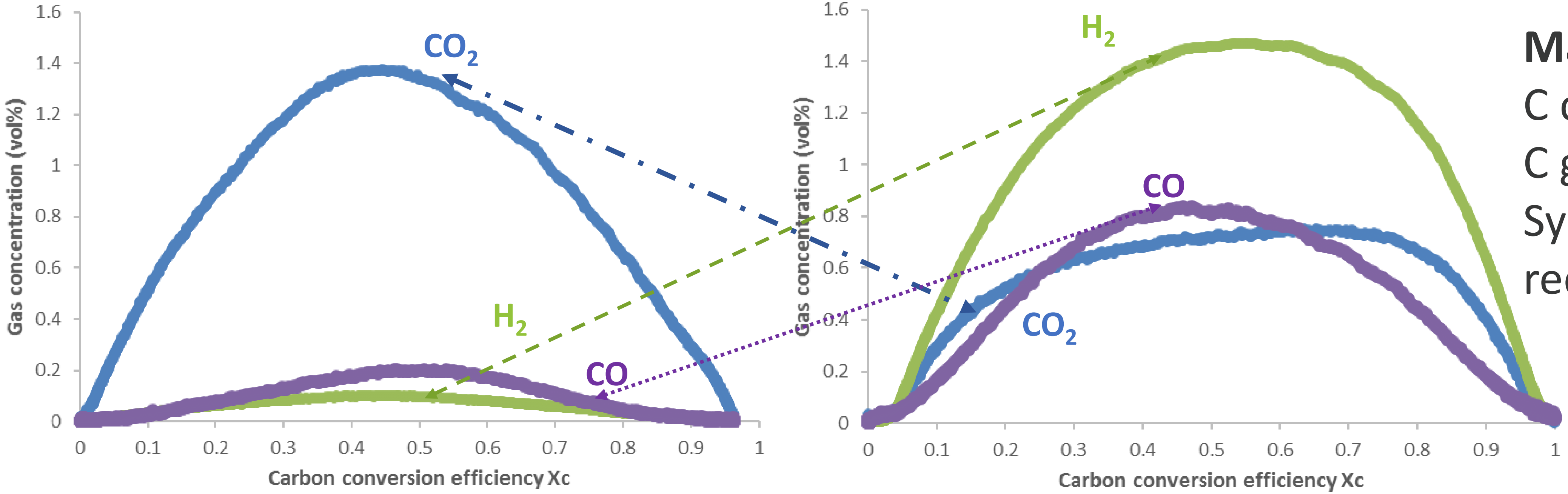


Carbon conversion rate dXc/dt

Fe40 OC with Coal Char in IG-CLC

CO_2 capture efficiency

- Mainly generated CO_2 at temperatures above 650°C
- Also produced CO + H_2 above 850°C
- Carbon capture efficiency η_{CO_2}=0.88 > η_{CO_2}=0.76 single Fe_2O_3 OC



Gas Concentrations of CO_2, CO and H_2 vs Xc in Fe40 OC and char reaction

Gas Concentrations of CO_2, CO and H_2 vs Xc in char gasification

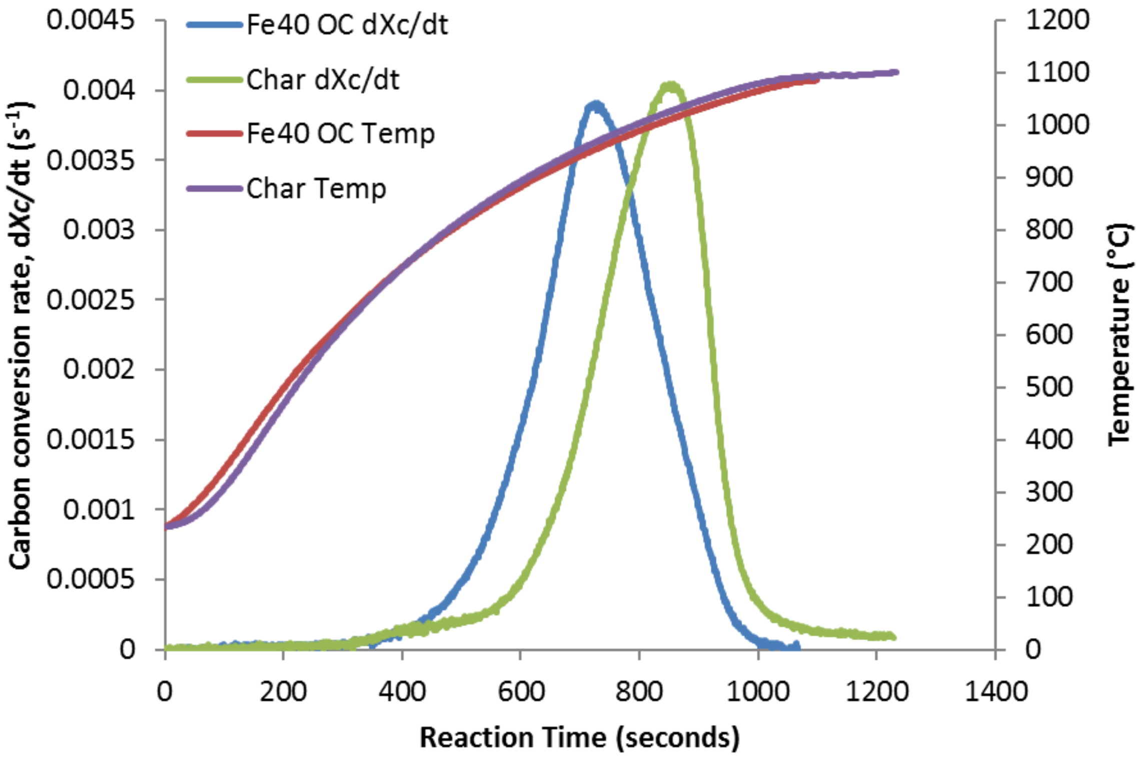
Main reactions

C combustion,
C gasification,
Syngas reduction

Fe40 OC with Coal Char in IG-CLC

Impact of reaction temperatures on the reactivity at φ 80

- Reaction rate increased as temperatures increased
- Reaction rate similar as temperature increased from 1000 to 1100°C



Carbon conversion rate dXc/dt of Fe40 OC with char and char gasification at 1100°C

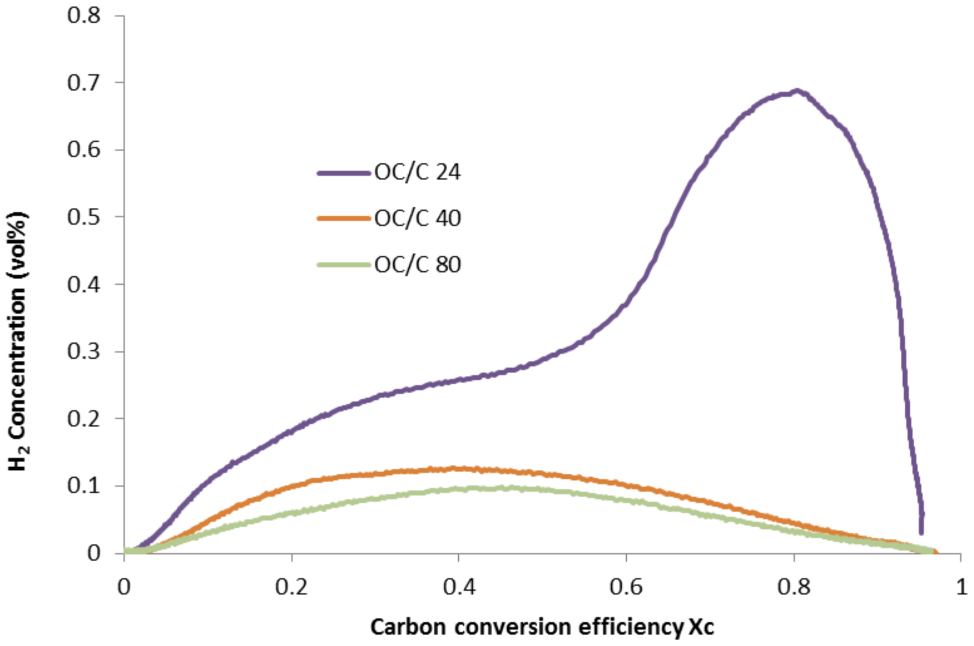
The maximum conversation rates and temperatures for Fe40 OC reactions with char and char gasification

Samples	Temp. (°C)	Rmax (s^{-1})	Tmax (°C)
Fe40 OC/char	950	0.0026	938
	1000	0.0037	966
	1100	0.0039	972
Char	950	0.0025	950
	1000	0.0036	988
	1100	0.0040	1026

Fe40 OC with Coal Char in IG-CLC

Impact ratios of OC to char on η_{CO_2} and OC phase changes

- Carbon capture efficiencies reduced as ratios of OC to char decreased due to increasing amount of CO and H_2
- $Cu^{2+}Fe^{3+}{}_2O_4 \xrightarrow[O_2]{} Cu^{+}Fe^{3+}O_2 \rightarrow Cu_xFe_{3-x}O_4$ (X=0.67 or 0.86) + Cu



Gas Concentrations of H_2 vs Xc at different ratios of Fe40 OC to char at 1000°C in Ar+H_2O

φ	η_{CO_2}	OC phase changes		
80	0.88	$Cu^{+}Fe^{3+}O_2$ (major)	$Cu_xFe_{3-x}O_4$* (major)	Cu (trace)
40	0.80	$Cu^{+}Fe^{3+}O_2$ (minor)	$Cu_xFe_{3-x}O_4$ (major)	Cu (minor)
24	0.76	NA	$Cu_xFe_{3-x}O_4$ (major)	Cu (minor)

* X=0.67 or 0.86

Main reactions

C combustion, C gasification, Syngas reduction

Cu40 OC and Coal Char in CLOU

Reactivity of Cu40 OC and char with φ 67 at 1000°C in Ar

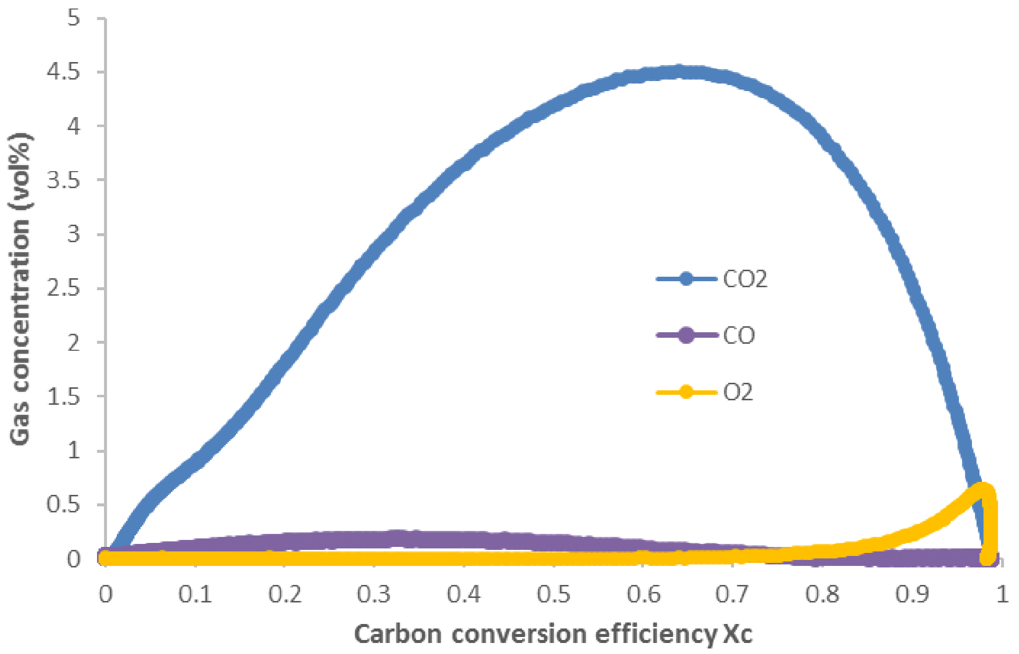
- Select φ 67 considering CuO/Cu_2O
- Xc= 0.99, Theoretical Xc= 1
- Maximum dXc/dt=0.0077 s^{-1} at Tmax=942°C
- Mainly generated CO_2 at temperatures above 650°C
- Carbon capture efficiency η_{CO_2}=0.96

Cu 40 OC phase changes

- CuO/Cu_2O
- $CuFe_2O_4/CuFeO_2$ ($Cu_2OFe_2O_3$)

Main reactions

C combustion, C partial combustion



Gas Concentrations of CO_2, CO and O_2 vs Xc

Cu40 OC and Coal Char Reactions in Ar+H_2O

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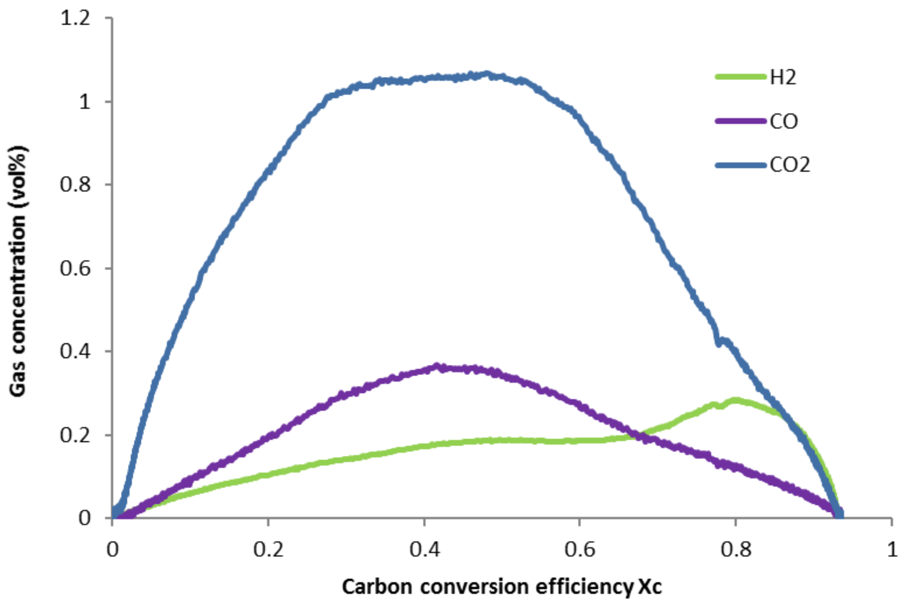
Impact ratios of OC to char on reactivity and OC phase changes

- Test results at φ 67 in Ar+H_2O are similar with ones at the same φ in Ar (CLOU)
- Test results at φ 18 are similar with the test of Fe40 OC and char at φ 24 in Ar+H_2O (IG-CLC)
- $Cu^{2+}O \rightarrow Cu^{+}{}_2O \rightarrow Cu$
- $Cu^{2+}Fe^{3+}{}_2O_4 \rightarrow Cu^{+}Fe^{3+}O_2 \rightarrow Cu_xFe_{3-x}O_4$ (X=0.67 or 0.86) + Cu



Gas Concentrations of CO_2, CO and H_2 vs Xc

φ	dXc/dt_{max} (s^{-1})	η_{CO_2}	OC phase changes			
67	0.0074 (CLOU)	0.94	Cu_2O major	$Cu^{+}Fe^{3+}O_2$ major	$Cu_xFe_{3-x}O_4$* trace	Cu NA
18	0.0031 (IG-CLC)	0.68	NA	NA	$Cu_xFe_{3-x}O_4$ major	Cu major

Summary

- Prepared Cu-Fe-Si OC for coal iG-CLC and CLOU formed $CuFe_2O_4$ and released gaseous O_2
- Ratios of oxygen carrier to char impact reactivity, CO_2 capture efficiency, and OC phases
- For coal iG-CLC using 40%Fe_2O_3+20%CuO+40%SiO_2 (by weight) oxygen carrier (Fe40 OC) at 1000^{o}C, char was fully converted with maximum carbon conversion rate $dXc/dt=0.0037\ s^{-1}$ at Tmax=956^{o}C and carbon capture efficiency $\eta_{CO_2}=0.88$ with CO and H_2
- For coal CLOU using 40%CuO+20%Fe_2O_3+40%SiO_2 (by weight) oxygen carrier (Cu40 OC) at 1000^{o}C, char was fully converted with maximum carbon conversion rate $dXc/dt=0.0077\ s^{-1}$ at Tmax=942^{o}C and carbon capture efficiency $\eta_{CO_2}=0.96$ with CO and O_2

Thank You

- Questions?
- Please contact Ping Wang
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