Application of Chemical Looping with Spouting Fluidized Bed for Hydrogen-Rich Syngas Production from Catalytic Coal Gasification

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Traditional Coal Gasification

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Limitations

- ASU & external water gas shift reaction
- Narrowed temperature range, and limited availability of sensible heat
- Extensive CH_4 and tar formation for low temperature gasification
- Low H_2 / CO ratio, and complicated process for slag discharge and waste water treatment

Characteristics of different gasification process

Process	Outlet Gas Temperature (°C)	Oxidant Demand	Steam Demand	Carbon Conversion	CH_4 concentration/ tar	H_2/CO (mol/mol)
Moving/fixed bed	425-650	low	high	low	>4% / high	2
Fluidized bed	900-1050	moderate	moderate	moderate	>2%/ low	0.6~0.7
Entrained flow	1250-1600	high	low	High>95%	<1000ppm/No	0.7

Project Objectives

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- **Develop an transformative catalytic coal gasification technology**
  - Avoid of ASU and external WGS
  - High temperature gasification to improve cold gas efficiency
  - Improve H_2/CO and eliminate CH_4 formation
- **Multi-function oxygen carrier development**
  - Oxygen & heat carrier
  - Catalyst to improve gasification and WGS reaction
- **Demonstration of novel spouted bed reactor**
  - Combination of gasification and WGS reaction
  - Avoid of ash melting
  - Ash separation

Why Red Mud – The Properties

Physical Characteristics

Particle size: **80% particles <10µm**

Concentration: **50-65%**

pH: 12-13.5(need neutralization)

No mechanical grinding & slurry preparation needed

Direct Granulation (spray dry method)

Calcination

Cost-effective OC

Chemical Composition(Dry)

No additive needed

- **Fe_2O_3:30%-60%**

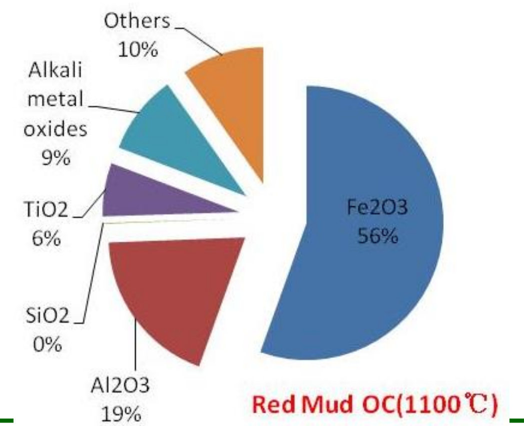
Active composition

- Al_2O_3:10%-20%
- SiO_2: 3%-50%
- TiO_2: 2%-25%

Support

- Na_2O: 2%-10%
- CaO: 2%-8%

Bonding



Catalytic Function for In-situ WGS

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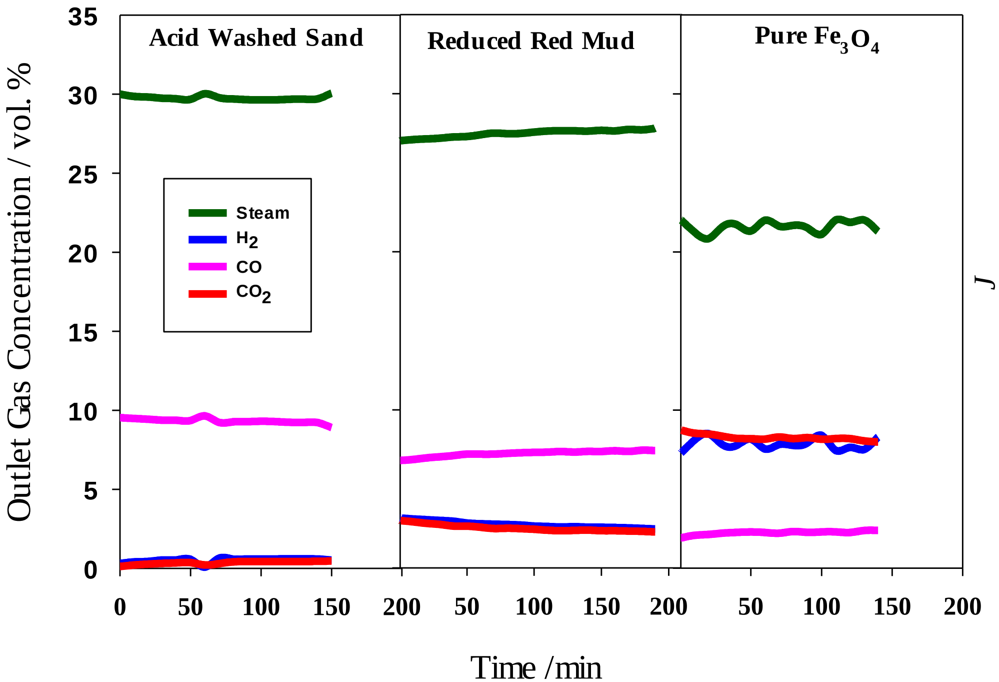

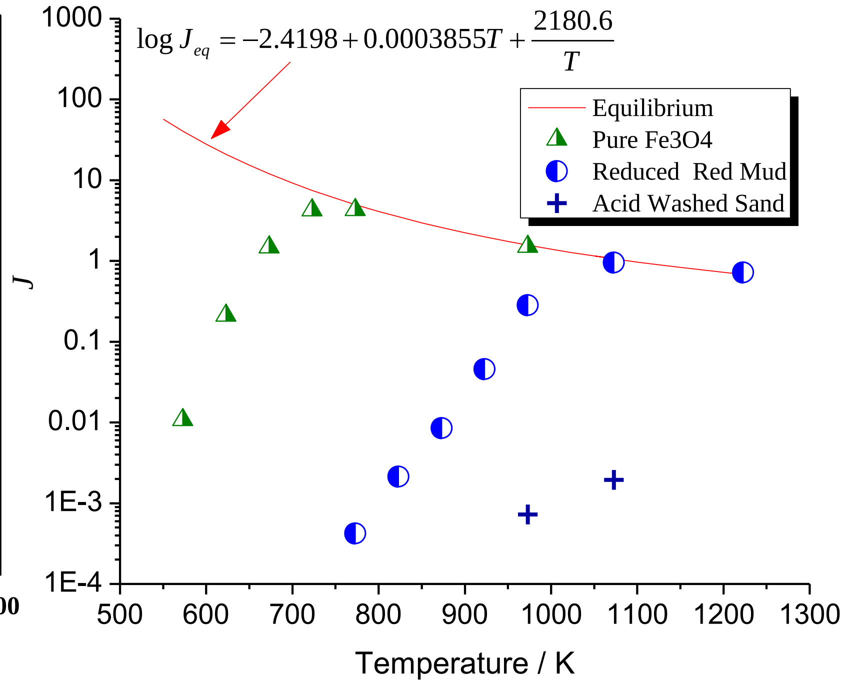

Gas residence time: 6s (973 K)

Inlet gas: 10% CO + 30% Steam

OC/Fuel Ratio

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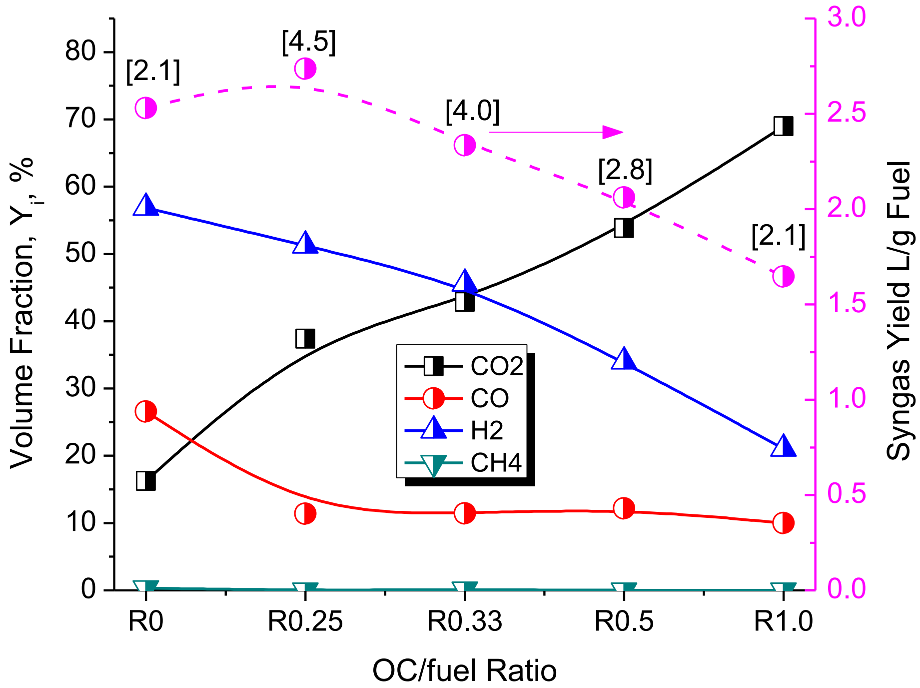
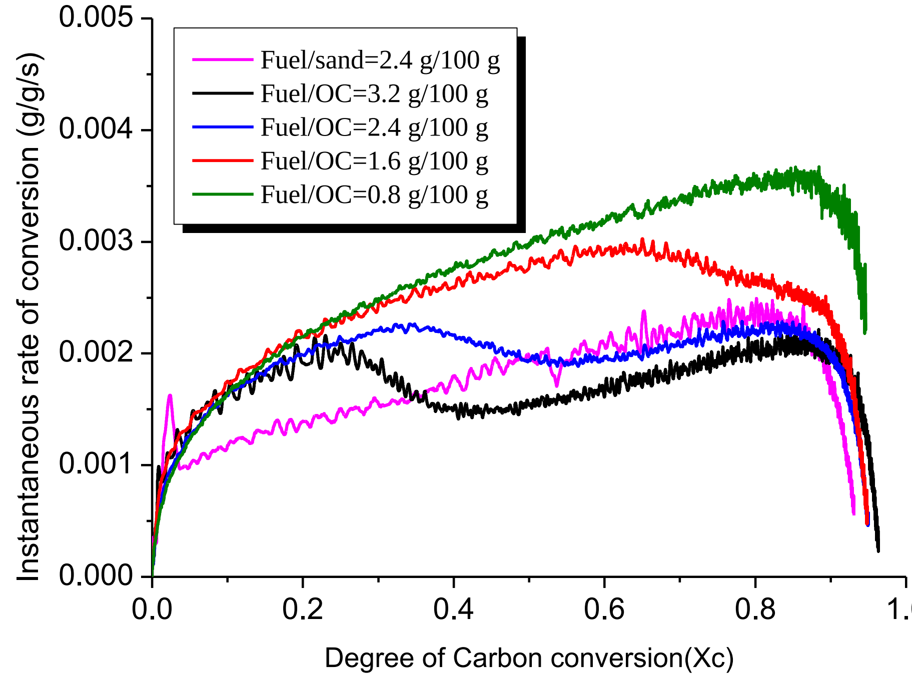
Gas Composition



Number in brackets : H_2/CO ratio

Fuel Conversion Rate



RM 100 g, Char 0.8-3.2 g
950 °C, 50 vol.% WV

Large Quantity Production

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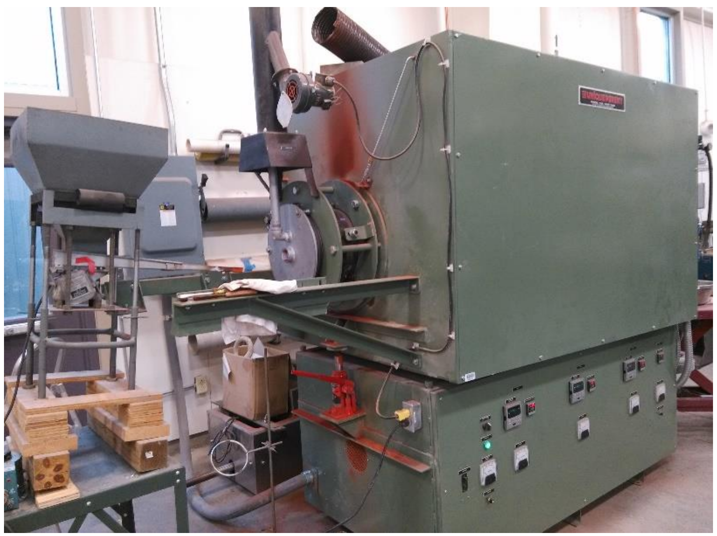
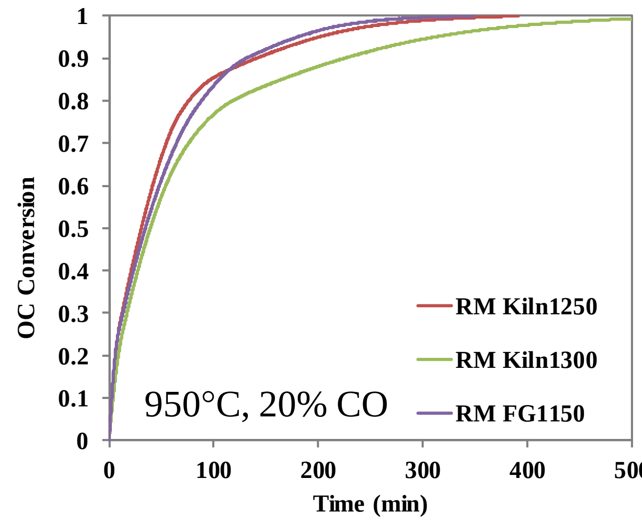
Raw Material → Fire in Kiln → Clinker → Crush Sieve → OC Product



Strength: 3.10 N

Cost: $87-113/ton



The Leachability

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- Water Leaching (ASTM D-3987)

	Alkaline Element			
	Na	K	Ca	Cl
Received	237.3	0.9	0.0	15.0
Calcined	36.4	3.8	3.3	1.2

pH(calcined)=11 < EPA limit 12.5

- Acid Leaching (TCLP - Toxicity Characteristic Leaching Procedure)

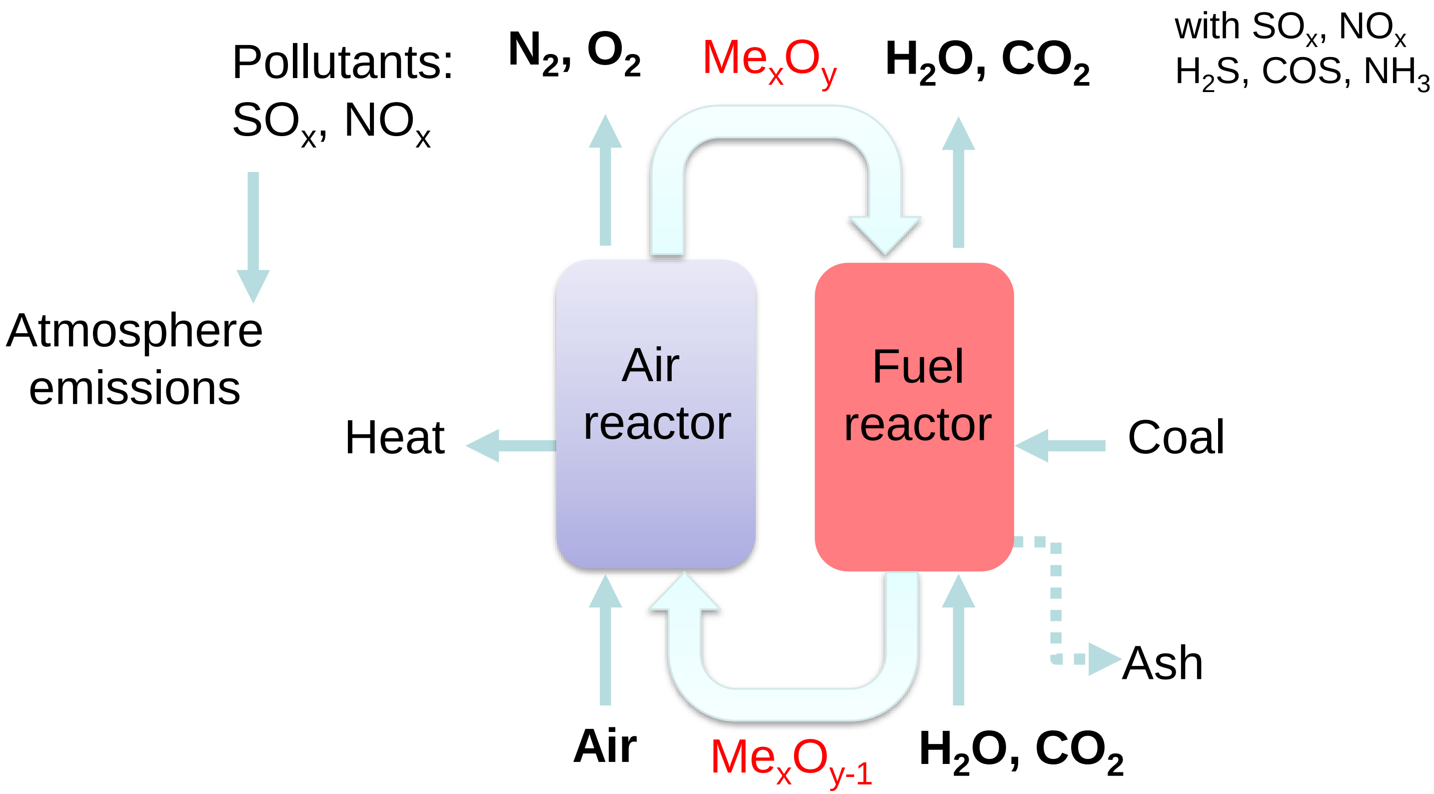
	Toxic Element							
	Cr	As	Se	Ag	Cd	Ba	Hg	Pb
Received	0.17	0.01	0.05	<0.01	<0.01	0.02	<0.001	<0.01
Calcined	0.38	0.02	0.05	<0.01	<0.01	0.04	<0.001	<0.01
EPA Limits	5	5	1	5	1	100	0.2	5

Grindability Comparison

			OPC		
Grind Time (min)	<125 um (g)	125-500 um (g)	>500 um (g)	Total Before Sieve (g)	Total After Sieve (g)
0	0	0	500	500	500
15	253	246	1	500	500
30	341	159	0	500	500
45	399	101	0	500	500
60	443	56	0	499	499
75	470	29	0	499	499
90	488	11	0	499	499
105	496	3	0	499	499
120	497	1	0	498	498

			RM		
Grind Time (min)	<125 um (g)	125-500 um (	>500 um (g)	Total Before Sieve (g)	Total After Sieve (g)
0	0	0	500	500	500
15	54	101	344	499	499
30	116	167	214	497	497
45	197	239	60	496	496
60	279	217	0	496	496
75	354	141	0	495	495
90	449	46	0	495	495
105	486	8	0	494	494
120	493	1	0	494	494

The Fate of Sulfur and Nitrogen



Composition of Coal and OCs

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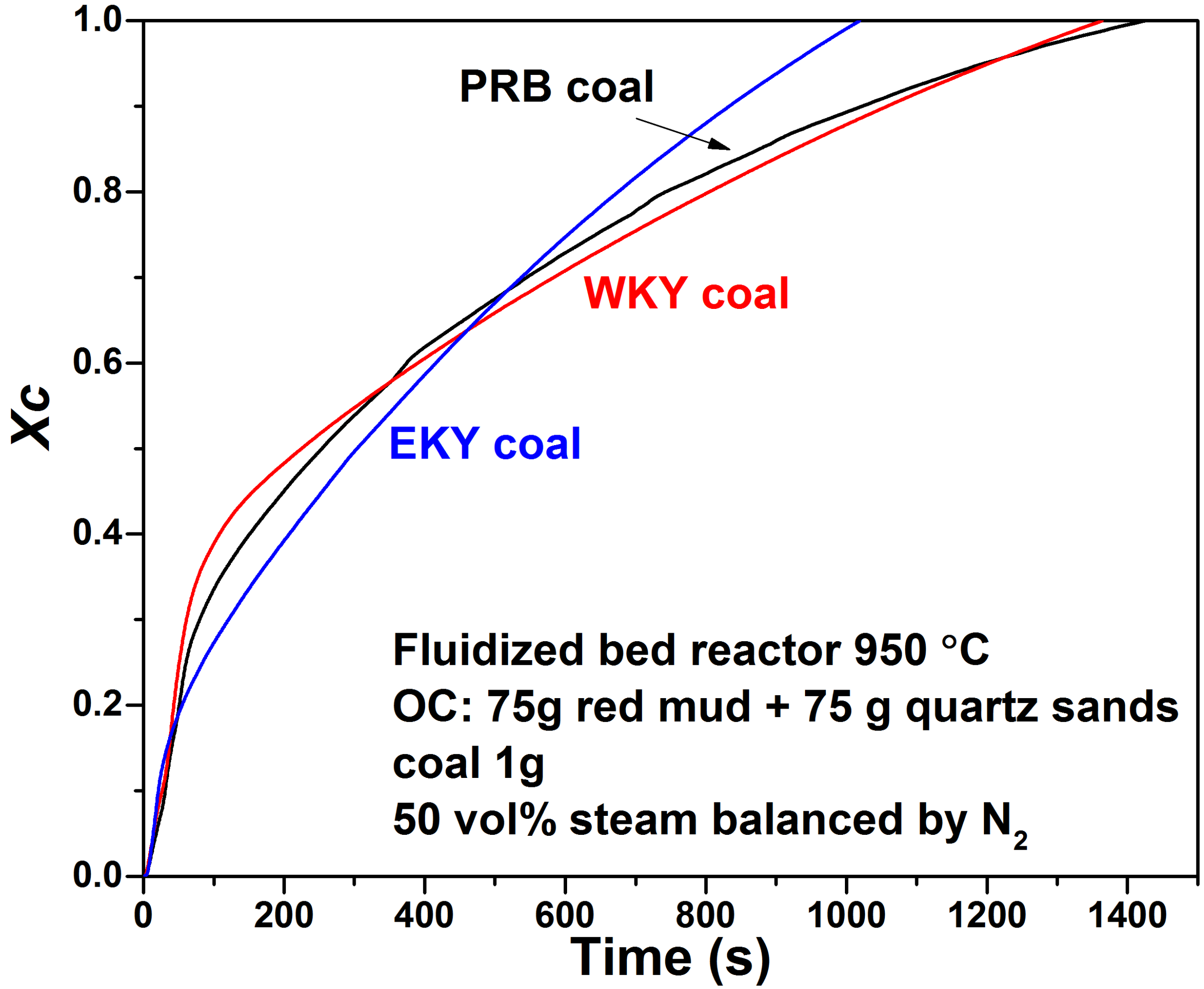
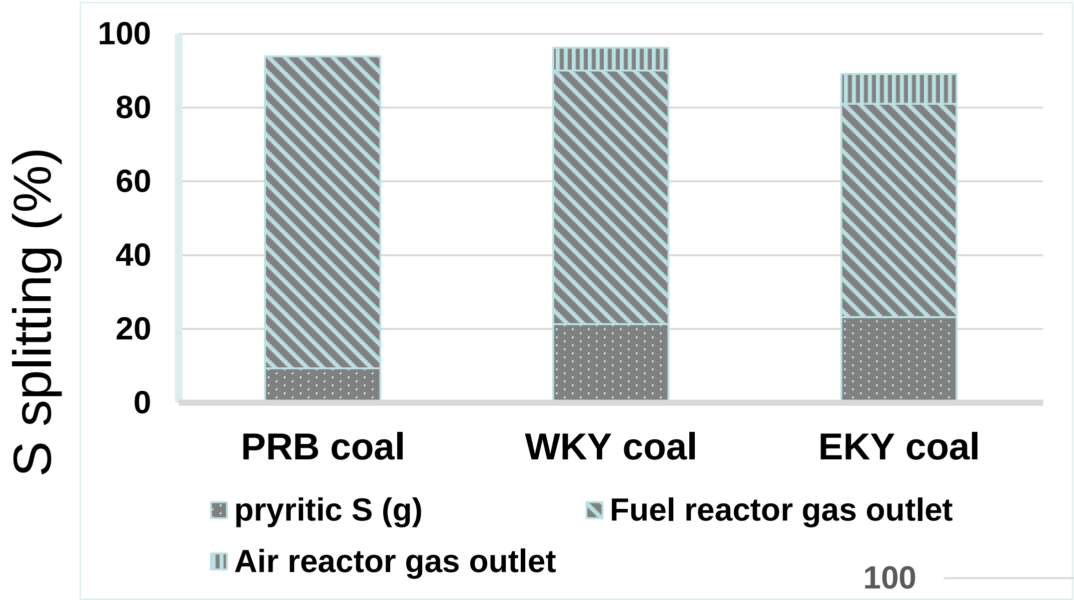
	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)					LHV (MJ/kg)
	Fixed Carbon	Volatile Matter	Moisture	Ash	C	H	O	N	S	
PRB	52.43	34.59	4.96	8.02	68.17	5.23	14.27	0.98	3.33	26.86
WKY	52.43	36.55	2.47	8.55	71.43	5.3	10.23	1.2	3.29	30.01
EKY	52.56	34.44	0.96	12.04	73.38	5.02	7.03	1.28	1.25	29.63

Red Mud Oxygen Carrier	
Fe_2O_3	43.74
Al_2O_3	23.37
SiO_2	11.78
TiO_2	7.74
CaO	5.54
Na_2O	6.43

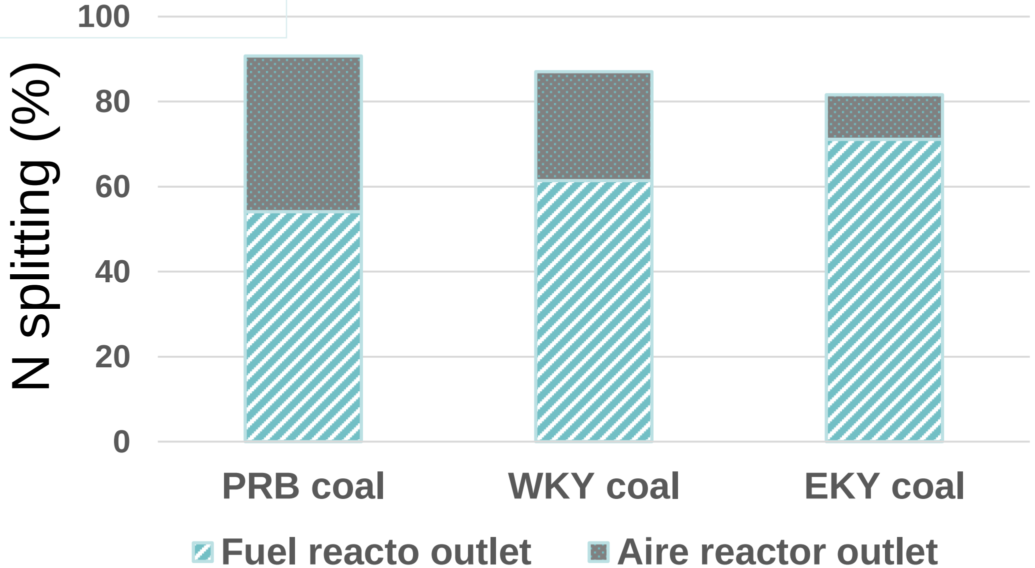
Operation to Ensure 100% Carbon Conversion



Sulfur and Nitrogen Balance



- Most S presented at the FR as SO_2
- In FR, more than 70% of total sulfur in coal



- N in coal exits as NO in FR and AR

No S- and N- Compounds in OCs

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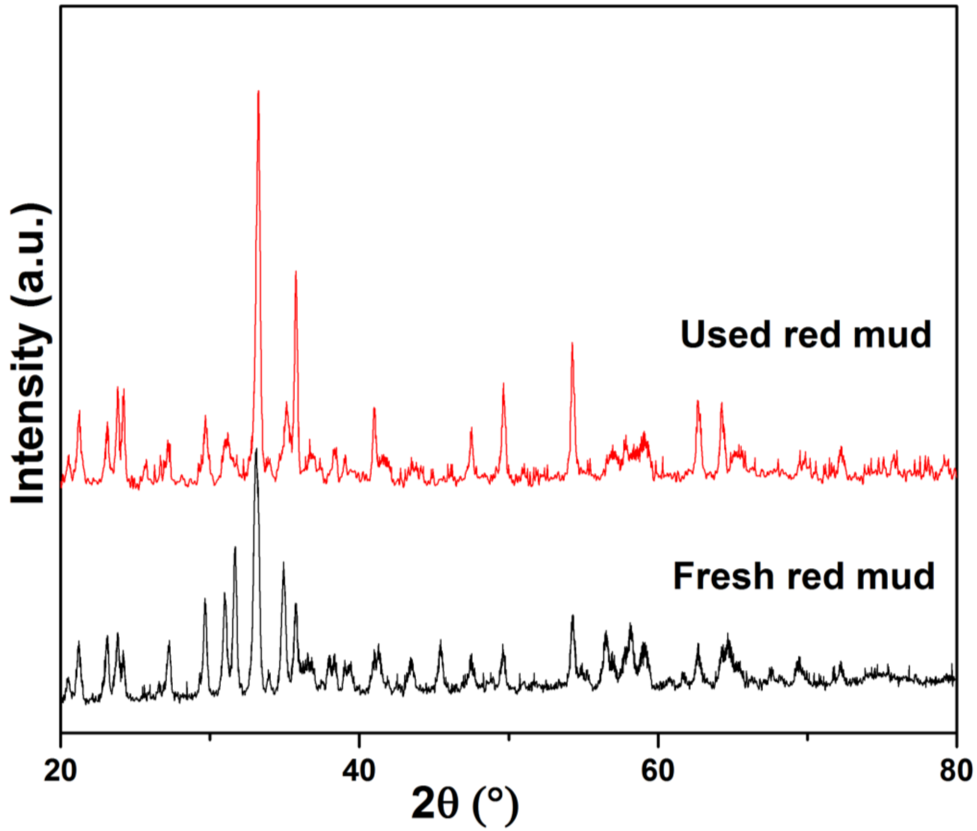

- No new phase generated, no sulfides or sulfates formed with red mud

50 KWth Unit

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Conclusions

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- Red mud is proven to be an effective oxygen carrier and catalyst for the CLG process. Stable reactivity is observed within 20 cycles. It also shows a good fuel selectivity.

- Gasification rate of char can be enhanced approximately by 1.5-3 times in the bed of red mud

- The effect of OC/fuel ratio on the produced syngas composition was studied. Syngas fraction increases when OC/fuel decreases due to oxygen lean condition.

- RM produced by rotary kiln displays a similar reactivity to RM synthesized by traditional freezing granulation method.
- The cost of RM produced by rotary kiln is estimated to be approximately $113 / ton.

Acknowledgements

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