Chemical-Looping Combustion of Solid Fuels
-
Status and recent progress

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GHGT-13

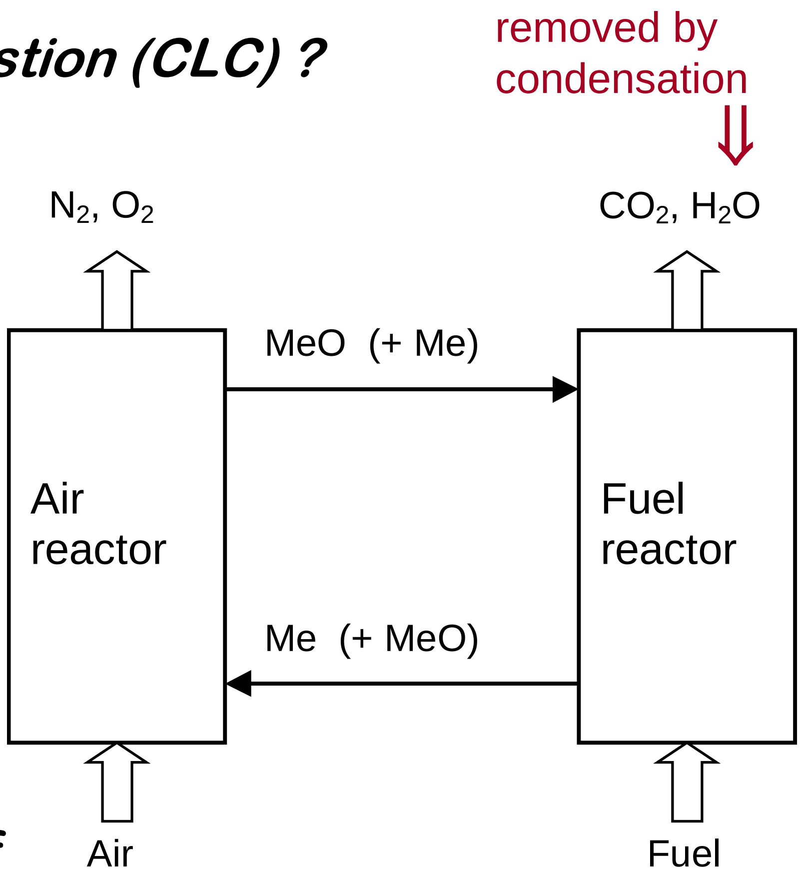
Lausanne, November 15-18, 2016

Why chemical-looping combustion (CLC) ?

Oxygen is transferred from air to fuel by metal oxide particles

Inherent CO_2 capture:

- **fuel and combustion air *never mixed***
- ***no active gas separation needed***
- **large costs/energy penalties of gas separation avoided**



- **Potential for real breakthrough in costs of CO_2 capture**

The oxygen carrier is the cornerstone of CLC

Overview CLC operation (150 publications)

	Reported operational time, h	Of which solid fuels
Manufactured materials:		
Nickel	3167	267
Copper	1036	158
Manganese	91	0
Iron	1652	1070
Cobalt	178	0
Combined oxides	718	106
Ores or waste materials:		
Iron	847	624
Ilmenite	1163	717
Manganese	243	158
Calcium sulfate	75	75
Total Manufactured	**6842**	**1601**
Total ores/waste	**2238**	**1574**
Total	**9170**	**3175**

>70 materials

Oxygen carriers

- Long experience of operation of a number of materials, in a number of different pilots, provides proof-of-concept
- Low cost materials (ores of ilmenite, manganese or iron) can be used with solid fuels, but less suitable for methane-rich gaseous fuels

Overview CLC units

Location	Unit	Oxides tested	Fuel\references	Year
Chalmers	10 kW-GL	NiO, Fe_2O_3, $CaMnO_3$, ilmenite	nat. gas, oil[1 2]	2004
KIER	50 kW	NiO, CoO	nat. gas[3]	2004
CSIC	10 kW	CuO, NiO	nat. gas[4]	2006
Chalmers	0.3 kW	NiO, Mn_3O_4, Fe_2O_3, CuO, ilmenite, $CaMnO_3$, Mn/Fe, Mn/Mg, Mn/Si, Mn/Fe/Si, Mn ore	nat. gas, syngas[5]	2006
Chalmers	10 kW–SF	ilmenite, Mn ore, $CaMnO_3$	coal, petcoke[6 7]	2008
CSIC	0.5 kW-GL	CuO, NiO, Fe_2O_3, $CaMnO_3$,	nat. gas, acid gas, sour gas, ethanol\[8]	2009
KAIST	1 kW	NiO + Fe_2O_3	CH_4\[9]	2009
Vienna UT	140 kW	ilmenite, NiO, CuO	nat. gas, CO, H_2[10]	2009
Alstom	15 kW	NiO	nat. gas\[11]	2009
Nanjing	10 kW –SF	NiO, Fe_2O_3	coal, biom.\[12]	2009
KIER	50 kW	NiO, CoO	nat.gas, syngas[13]	2010
Nanjing	1 kW – SF	Fe_2O_3 (ore)	coal, biomass, sewage sludge[14 15]	2010
IFP-Lyon	10 kW-GSF	NiO, CuO, Mn ore	CH_4 ,coal, syngas[16 17]	2010
Stuttgart	10 kW	ilmenite	syngas[18]	2010
Xi'an Jiaotong	10 kW- Pr	CuO/Fe_2O_3	coke oven gas[19]	2010
CSIC	1.5 kW-SF	ilmenite, CuO, Fe_2O_3	coal[20]	2011
Chalmers	0.3 kW LF	NiO, Mn_3O_4, CuO	kerosene\[21]	2011
Chalmers	100 kW – SF	ilmenite, Fe ore, Mn ore	coal, petcoke, wood char[22 23]	2012
Hamburg	25 kW –SF	ilmenite	coal, CH_4\[24]	2012
Ohio	25 kW –SF	Fe_2O_3	coal[25 26]	2012
Nanjing	50 kW-Pr-SF	iron ore	coal[27]	2012
Tsinghua	0.2 kW	ilmenite	CO[28]	2013
Darmstadt	1 MW –SF	ilmenite	coal[29 30]	2015
Alstom	3 MW –SF	$CaSO_4/CaS$	coal[31]	2014
CSIC	50 kW-SF	ilmenite, iron ore, $CuO/Fe_2O_3/MgAl_2O_4$	coal, lignite, anthracite[32]	2014
Huazhong	5 kW-GSF	iron ore	CH_4 coal[33]	2015
Guangzhou	10 kW-G	Fe_2O_3	saw dust[34]	2015
Nanjing	25 kW-G	NiO, iron ore	rice husk[35]	2015
KIER	200 kW	NiO	nat. gas[36]	2016
Huazhong	5 kW-SF	iron ore	coal[37]	2016
Sintef	150 kW	CuO	CH_4[38]	2016
VTT	20 kW-SF	ilmenite	biomass[39]	2016
NETL	50 kW	CuO/Fe_2O_3	CH_4[40]	2016
Chalmers	1.4/10 MW-SF	ilmenite, Mn ore	biomass[41]	2016

SF-solid fuel, GSF-gaseous & solid fuel, Pr-pressurized, LF-liquid fuel, GL=gaseous/liquid fuel, G-Gasification

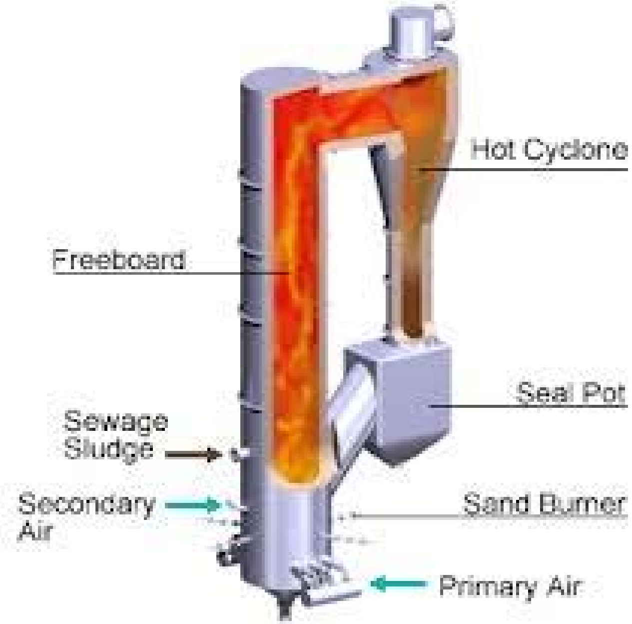
34 CLC units

18 units for solid fuels (including 2 gasifiers)

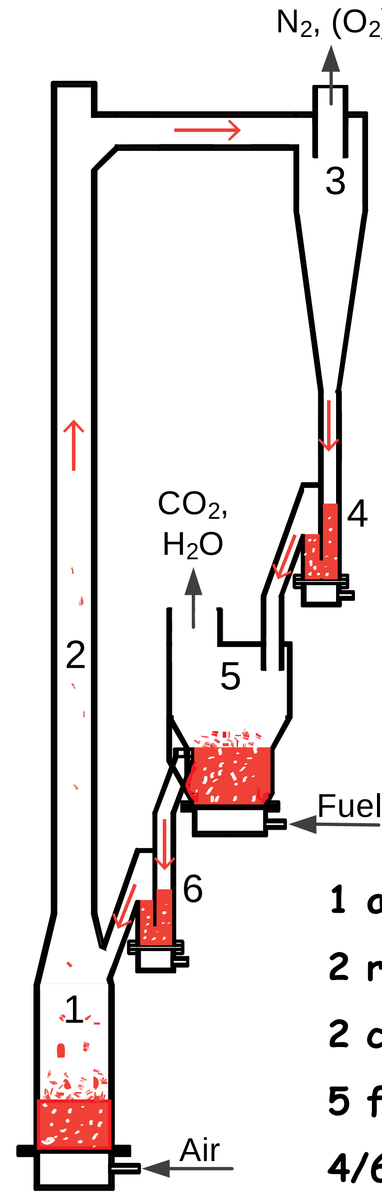
Size range 0.2 kW – 3 MW

Dual fluidized beds, except Ohio, moving bed.

Circulating fluidized bed (CFB) combustion technology is common for burning solid fuels.



Example: 10 kW CLC pilot for gaseous fuel (2003)



1 air reactor

2 riser

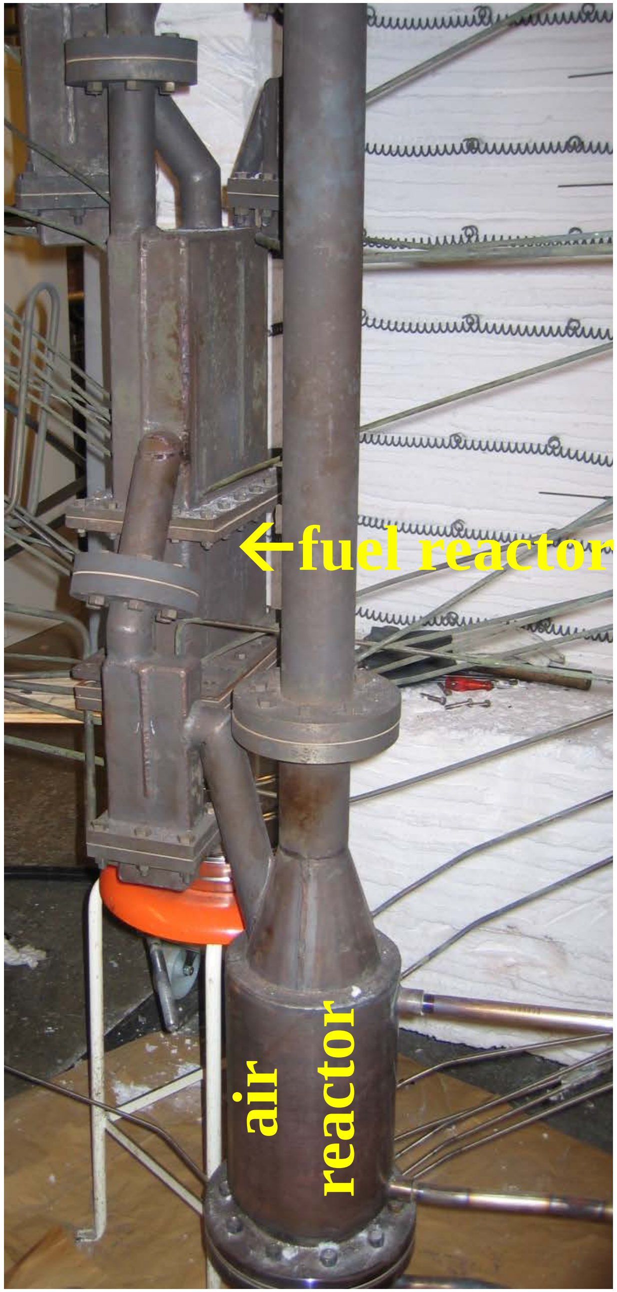
2 cyclone

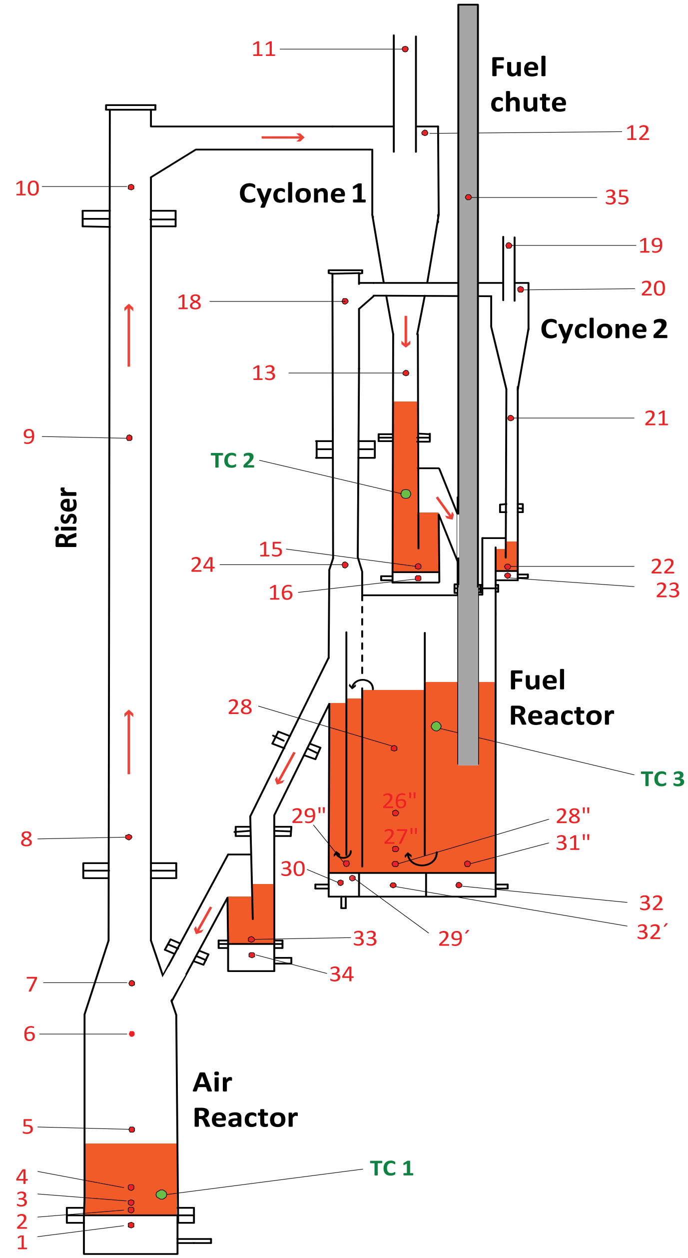
5 fuel reactor

4/6 loop seals

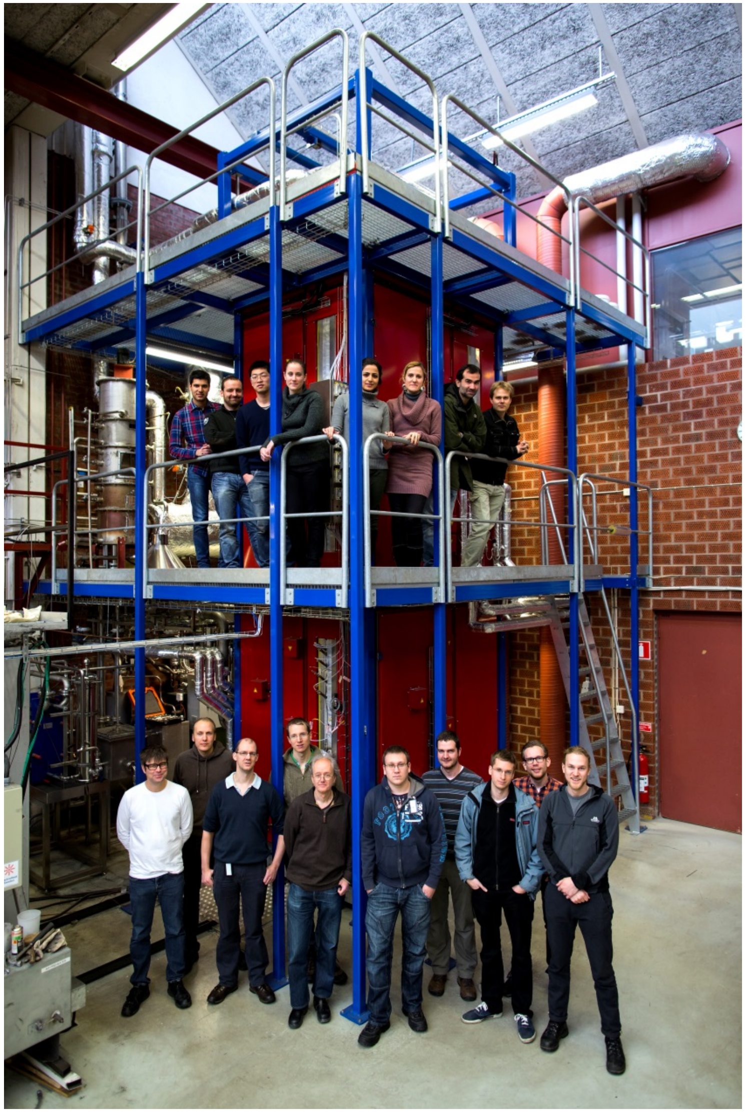
CLC uses CFB principle to circulate bed material. The principal difference is adding a fuel reactor on the return side.

Chalmers' 10 kW chemical-looping combustor for solid fuels, 2006



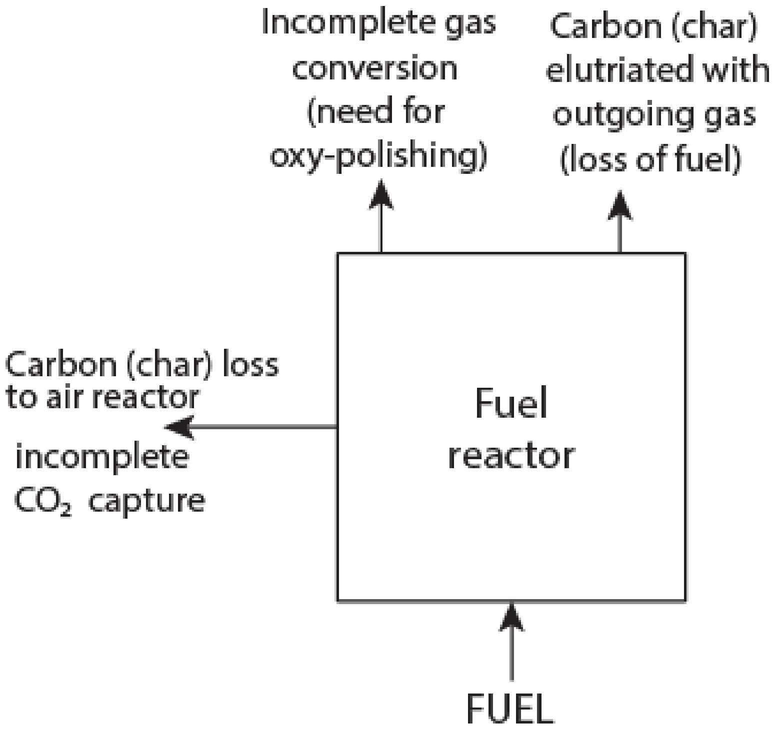


Chalmers’ 100 kW CLC for solid fuel, publ. 2012

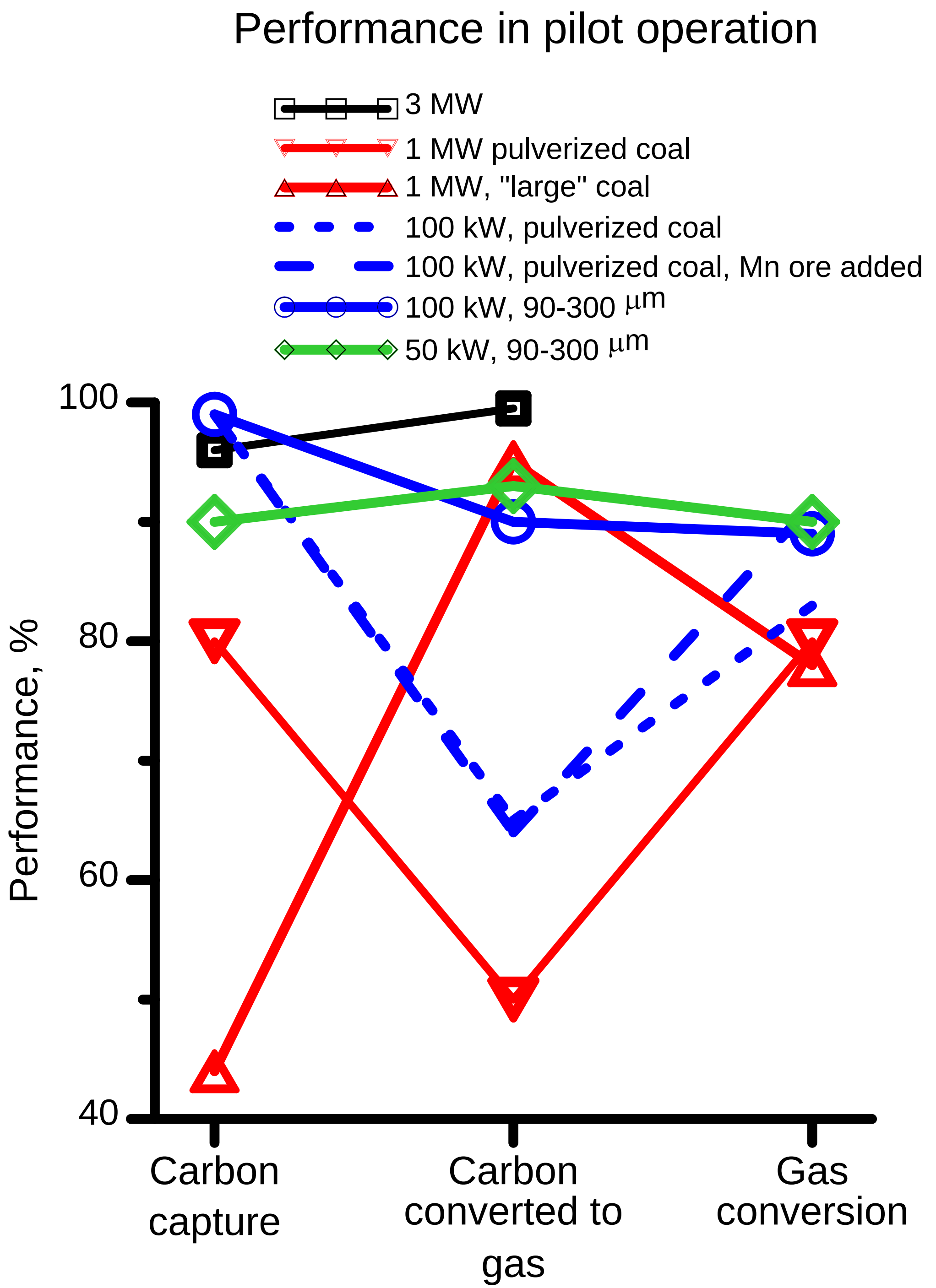


Operation with solid fuels –
3 causes for incomplete fuel conversion

- Gas not fully oxidized to CO_2/H_2O
  - oxygen needs to be added after fuel reactor
- Fine char particles lost from fuel reactor
  - added cost of fuel, increased waste disposal.
- Char follows particle flow to air reactor.
  - CO_2 capture not complete.



⇒ 3 performance criteria:
⇒ 1) gas conversion
⇒ 2) carbon conversion to gas
⇒ 3) CO_2 capture


Performance in pilot operation
3 MW
1 MW pulverized coal
1 MW, "large" coal
100 kW, pulverized coal
100 kW, pulverized coal, Mn ore added
100 kW, 90-300 μm
50 kW, 90-300 μm
Performance, %
100
80
60
40
Carbon capture
Carbon converted to gas
Gas conversion

Fuel size:

- Avoid fines, e.g. pulverized coal, for low carbon loss
- Avoid larger particles, e.g. pulverized coal, for high CO_2 capture
- Intermediate sized coal, 100-300 mm, likely optimal

Scale-up

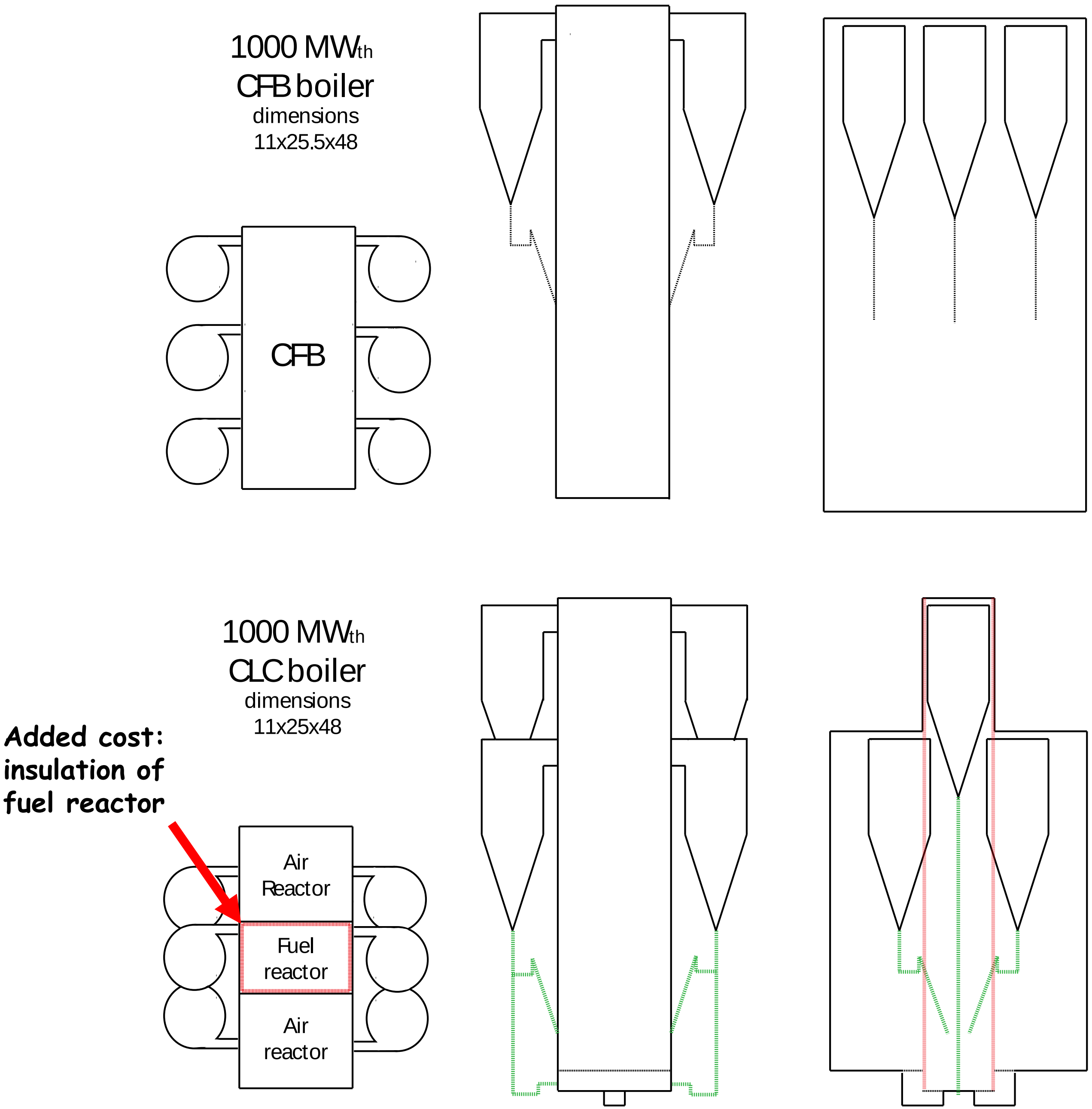
Full scale expected to :

- reduce loss of carbon fines significantly because of increased residence time
  - High riser
  - Better cyclone efficiency
- improve gas-solids contact in riser
- reduce gas-solids contact in bottom bed

But …

Incomplete gas conversion difficult to avoid

- Downstream oxygen polishing likely best way to reach full conversion
- Oxygen need expected to be 5-10 times less than in oxyfuel



Fuel reactor, cyclones, ducts and post-oxidation chamber: 2500 m^2

Cost: 1500 €/m^2

Added cost of fuel reactor:

4 M€

$\Rightarrow$ 0.4 M€/year

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2 Mton CO_2/year

= 0.2 €/ton CO_2

From: Lyngfelt, A., and Leckner, B., A 1000 MWth Boiler for Chemical-Looping Combustion of Solid Fuels - Discussion of Design and Costs, *Applied Energy* in press *(available on-line)*

Other costs

- CO_2 compression
  - Similar to other capture technologies
- Oxygen production (incomplete conversion)
  - 5-10 times less oxygen compared to oxyfuel
- CO_2 purification
  - As in oxyfuel, option for SO_2/NO_x capture
- Oxygen carrier
  - With low cost ores, estimated to 1-4 €/tonne CO_2
- Minor costs, >1 €/tonne
  - Fuel grinding, steam for fluidization
- Total costs, estimated to 16-26 €/tonne CO_2

Strategy for full-scale demonstration of chemical-looping at low cost ?

Build dual purpose CFB/CLC, or retrofit CFB to CLC

- Low added cost of CLC plant

Skip CO_2 capture (in 1st stage)

- Major added costs can be avoided, i.e. CO_2 compression and purification, and oxygen production

Go for biomass

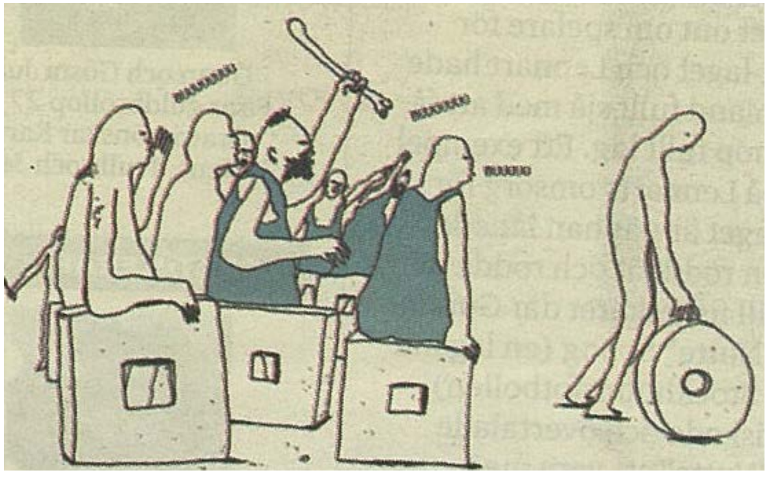
- Potential advantages for avoiding fouling/high-temperature corrosion, thus potential of higher steam data/higher efficiency. Pollutants (NO_x) in smaller CO_2 stream, emissions can be reduced

When the technology successfully demonstrated, add CO_2 capture (2nd stage)

Conclusions

- **>9000 h of operation and >3000 h with low-cost mtrls shows CLC is feasible**
  - Good performance can be reached in pilots, and expected to improve in large scale
  - Incomplete gas conversion can be addressed by ”oxy-polishing”
- **Significant cost reduction because little gas separation needed**
- *Technology is ready for scale-up !*

THANK YOU !
QUESTIONS ?



>300 CLC publications at:

http://www.entek.chalmers.se/lyngfelt/co2/co2publ.htm