Chemical-Looping Combustion of Solid Fuels
-
What is Needed to Reach Full-Scale ?

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4th International Conference on Chemical Looping

Southeast University

Nanjing, September 26-28, 2016

Overview

- Operational experiences.
- Performance criteria
- Scale-up discussion

Overview CLC operation (150 publications)

	Reported operational time, h	Of which solid fuels
Manufactured materials:		
Nickel	3067	267
Copper	822	158
Manganese	91	0
Iron	1652	1070
Cobalt	178	0
Combined oxides	646	74
Ores or waste materials:		
Iron	775	552
Ilmenite	1085	639
Manganese	183	74
Calcium sulfate	75	75
Total Manufactured	**6456**	**1569**
Total ores/waste	**2118**	**1340**
Total	**8574**	**2909**

>70 materials

The oxygen carrier is the cornerstone of CLC

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
- Copper-based materials with oxygen release (CLOU) would be excellent for solid fuels, except for cost
- Manganese oxides combined with Fe, Si, Ca … shows some CLOU property. Mn ores normally contain Fe and Si. Combined Mn materials have less endothermic, or exothermic, reactions in fuel reactor.
- Manganese ores generally appear more reactive than ilmenite, but higher attrition may give shorter lifetime.

Overview CLC units

Location	Unit	Year
Chalmers	10 kW	2004
KIER	50 kW	2004
CSIC	10 kW	2006
Chalmers	0.3 kW	2006
Chalmers	10 kW–SF	2008
CSIC	0.5 kW	2009
KAIST	1 kW	2009
Vienna UT	140 kW	2009
Alstom	15 kW	2009
Nanjing	10 kW –SF	2009
KIER	50 kW	2010
Nanjing	1 kW – SF	2010
IFP-Lyon	10 kW-GSF	2010
Stuttgart	10 kW	2010
Xi'an Jiaotong	10 kW- Pr	2010
CSIC	1.5 kW-SF	2011
Chalmers	0.3 kW LF	2011
Chalmers	100 kW – SF	2012
Hamburg	25 kW –SF	2012
Ohio	25 kW –SF	2012
Nanjing	50 kW-Pr SF	2012
Tsinghua	0.2 kW	2013
Darmstadt	1 MW –SF	2014
Alstom	3 MW –SF	2014
CSIC	50 kW-SF	2014
Huazhong	5 kW-G/SF	2015
Guangzhou	10 kW-G	2015
Nanjing	25 kW-G	2015

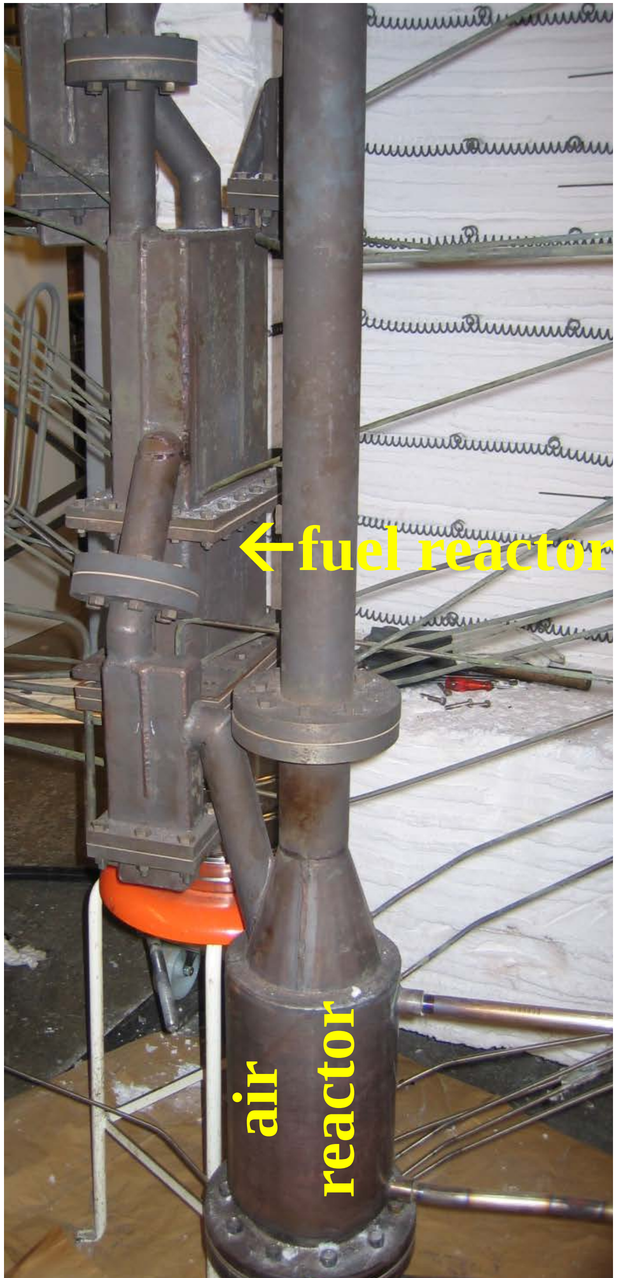
SF-solid fuel, GSF-gaseous & solid fuel, Pr-pressurized,
LF-liquid fuel, G-Gasification

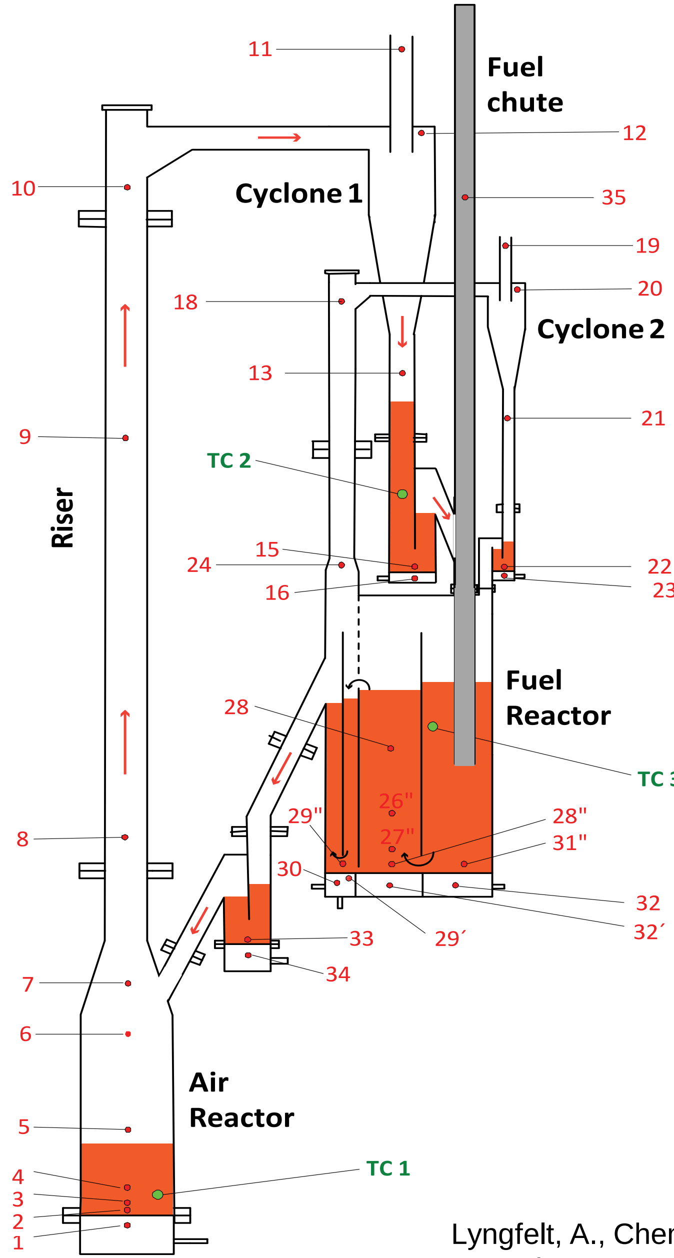
28 CLC units
+ some new units presented at this conference

15 units for solid fuels (including 2 gasifiers)

Size range 0.2 kW – 3 MW

Dual fluidized beds, except Ohio, moving bed.





Chalmers' 10 kW chemical-looping combustor for solid fuels.

First operation 2006

Published 2008

Lyngfelt, A., Chemical-looping combustion of solid fuels, *Greenhouse Gas Issues*, No. 87, September 2007, 9-10.

Southeast University, Nanjing 10 kW solid fuel

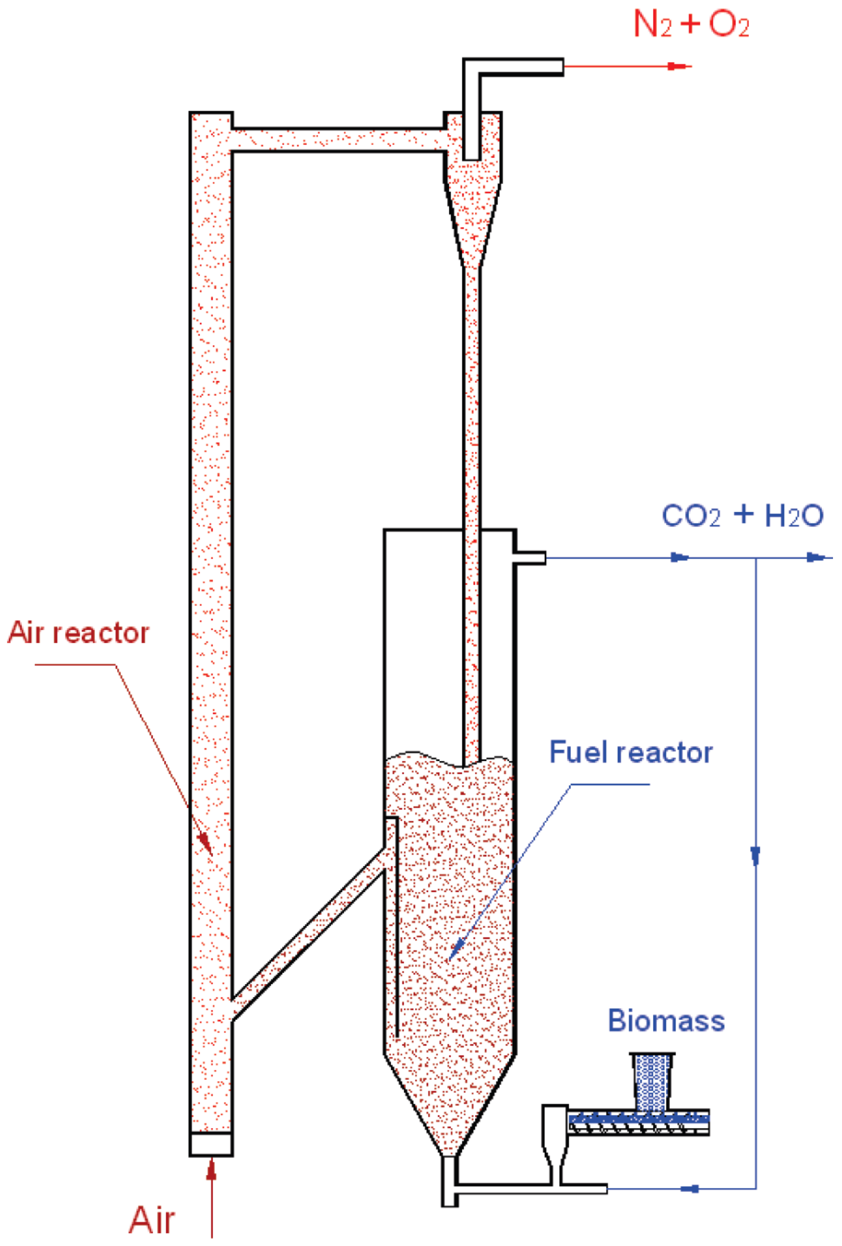
Dimensions:

- AR: Ø 5 cm, height 2 m
- FR: 23x4 cm, height 1.5 m

Type:

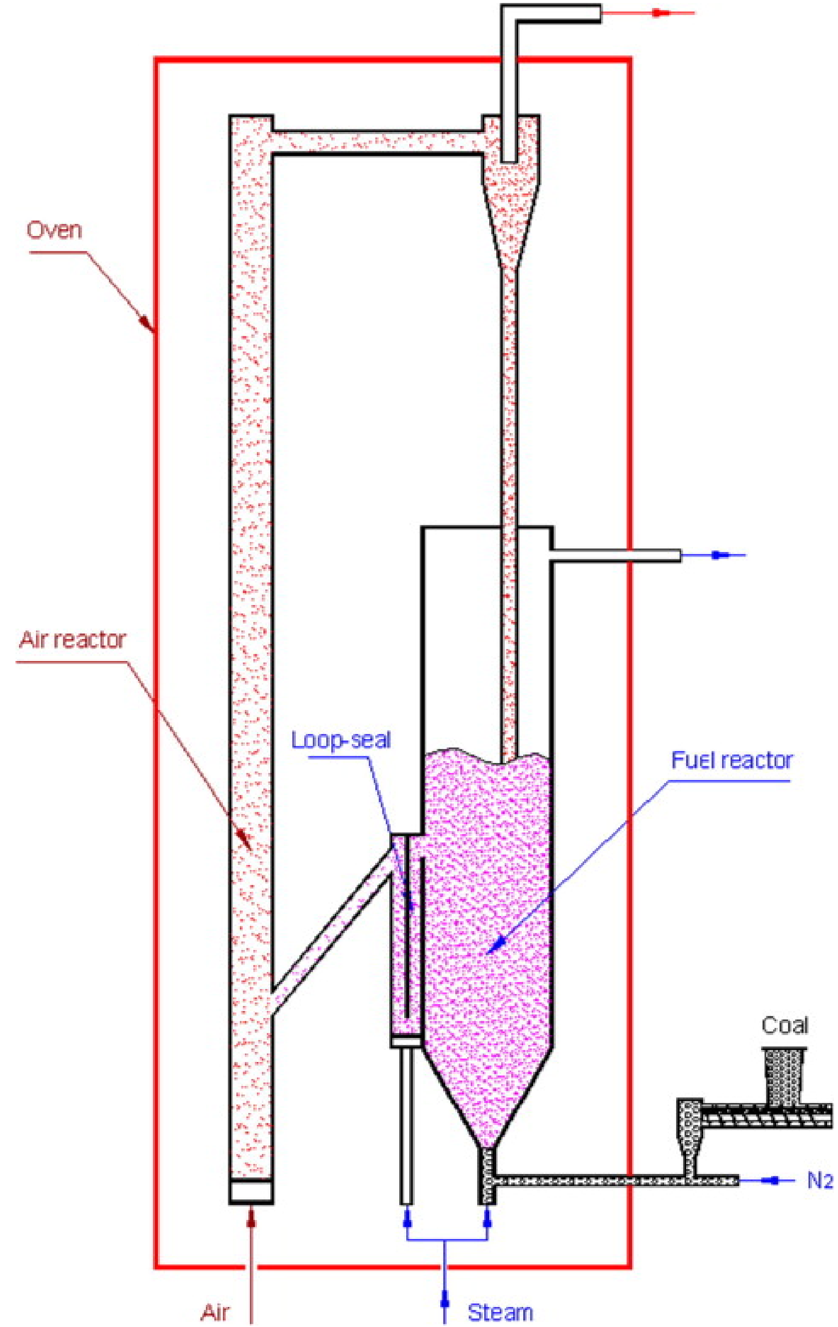
- Circulating AR
- Spouted FR, outflow via a special direct connection to AR

First published: 2009

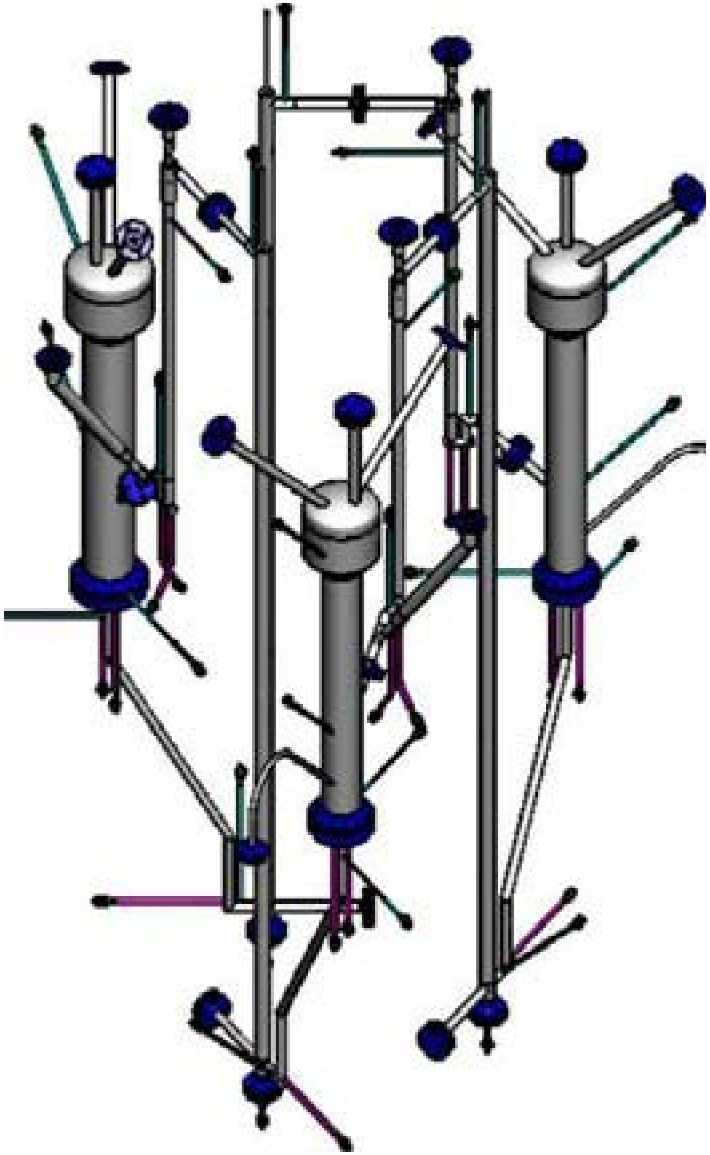


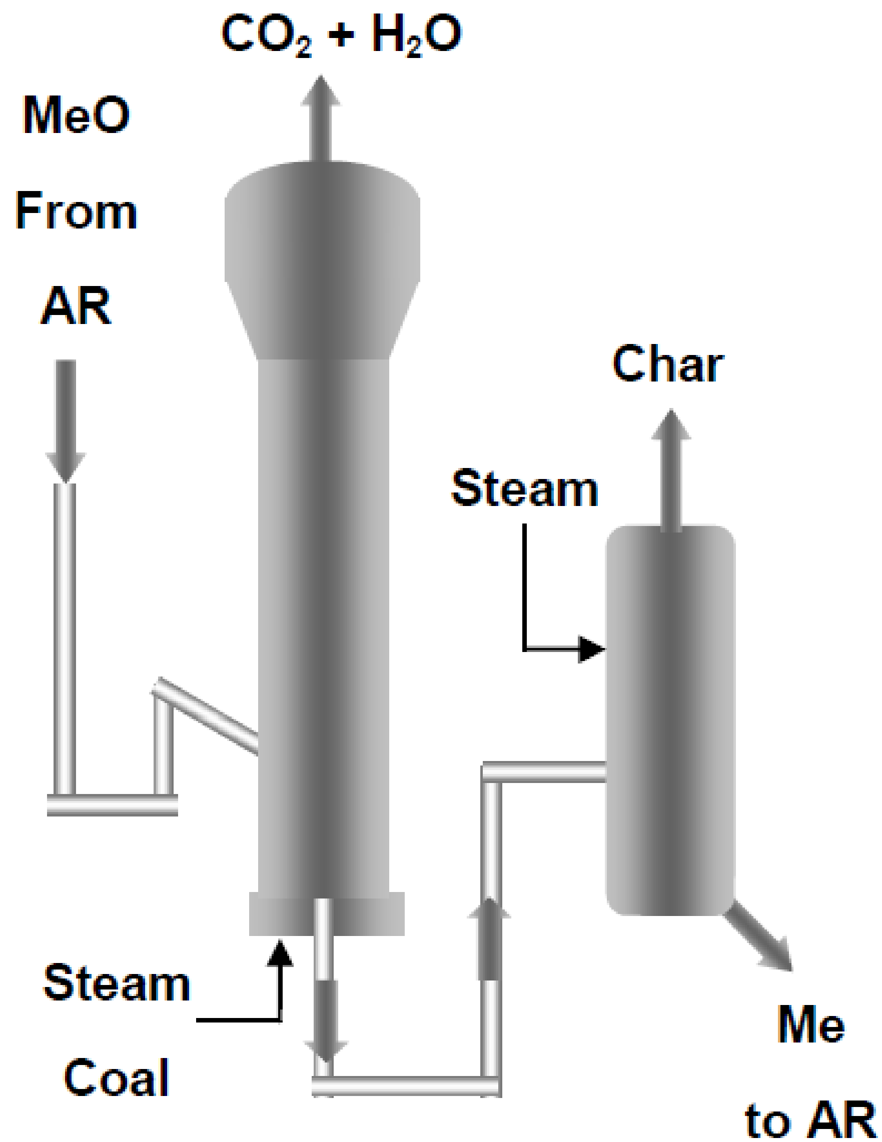
Nanjing 1 kW
Publ. 2010

Loopseal modified

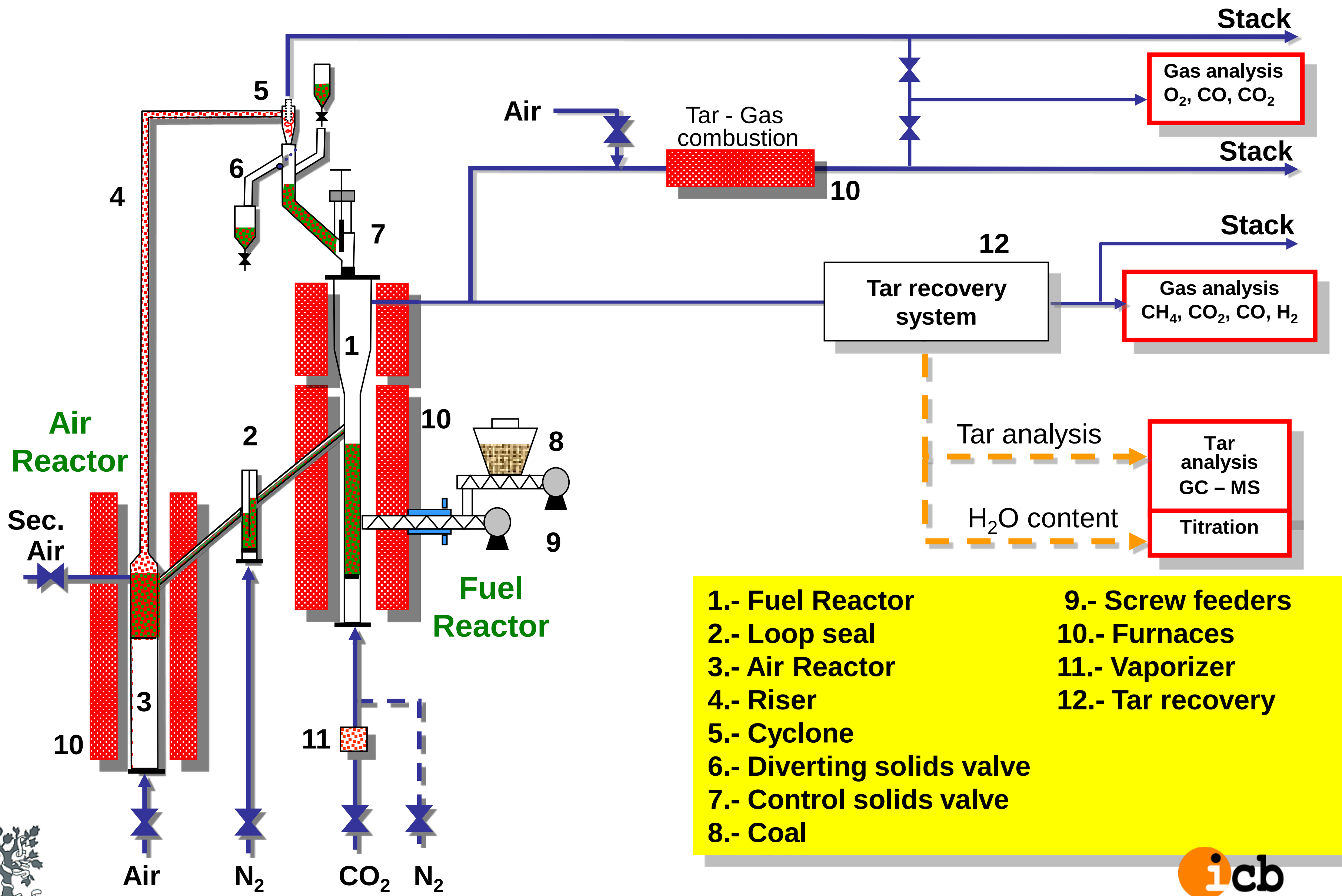


IFP, France, 10 kW gas / solid fuel unit, publ. 2010





CSIC 0.5-1.5 kW CLC for solid fuels, publ. 2011



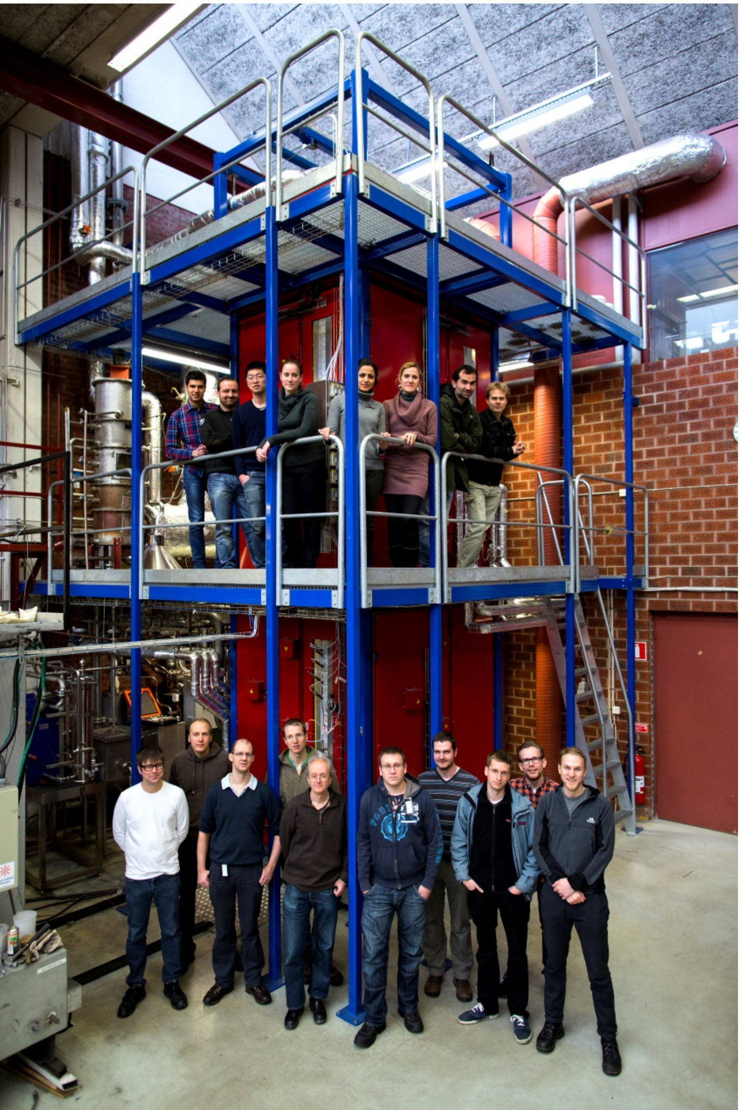
CSIC

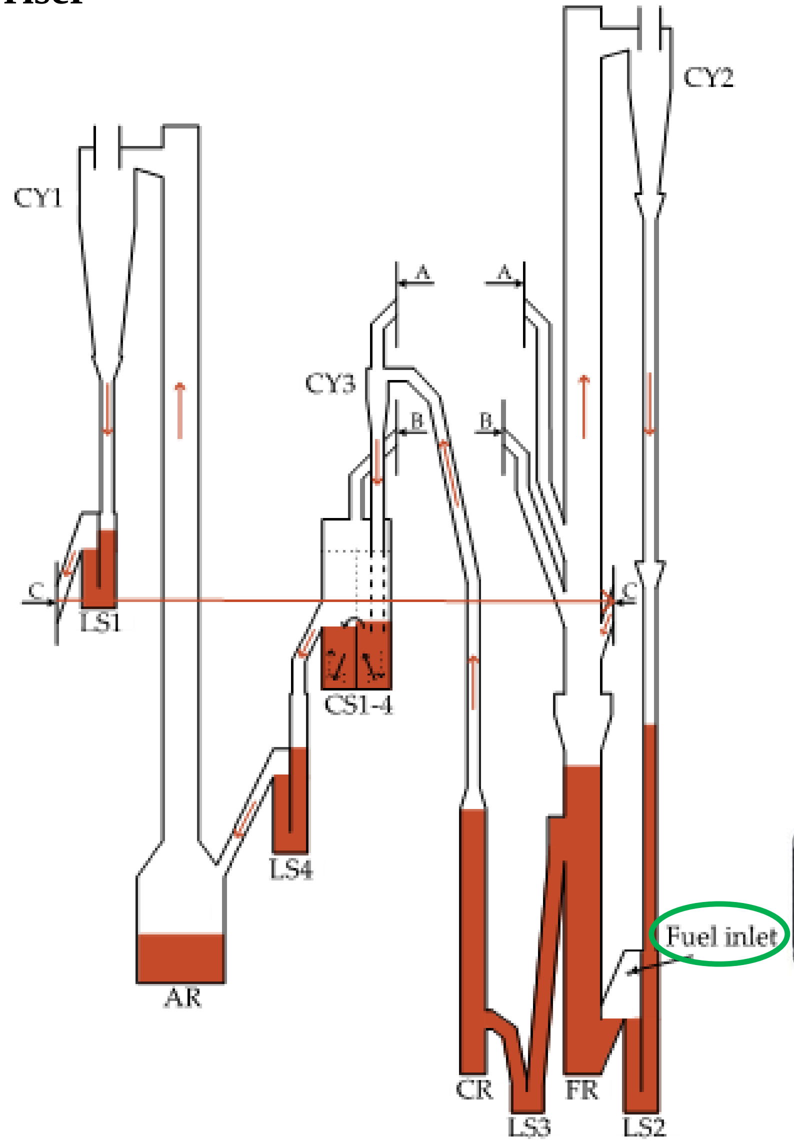
icb INSTITUTO DE CARBOQUIMICA

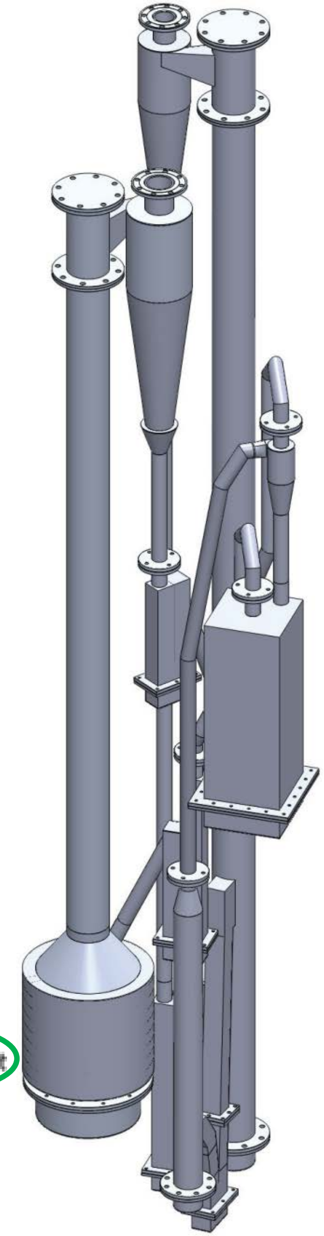
Chalmers’ 100 kW CLC for solid fuel, publ. 2012

AR=Air reactor, FR=fuel reactor, LS=loop seal, C=cyclone,

CS=Carbon stripper, CR=Circulation riser

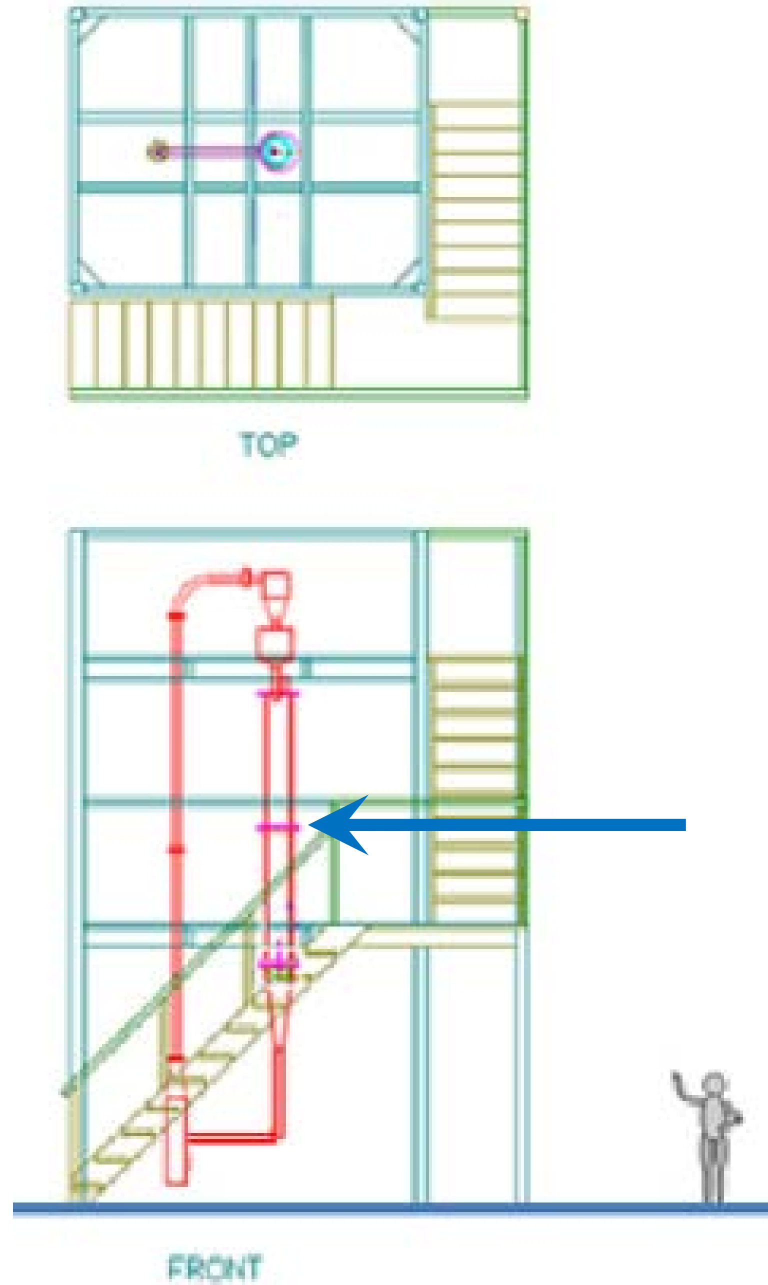




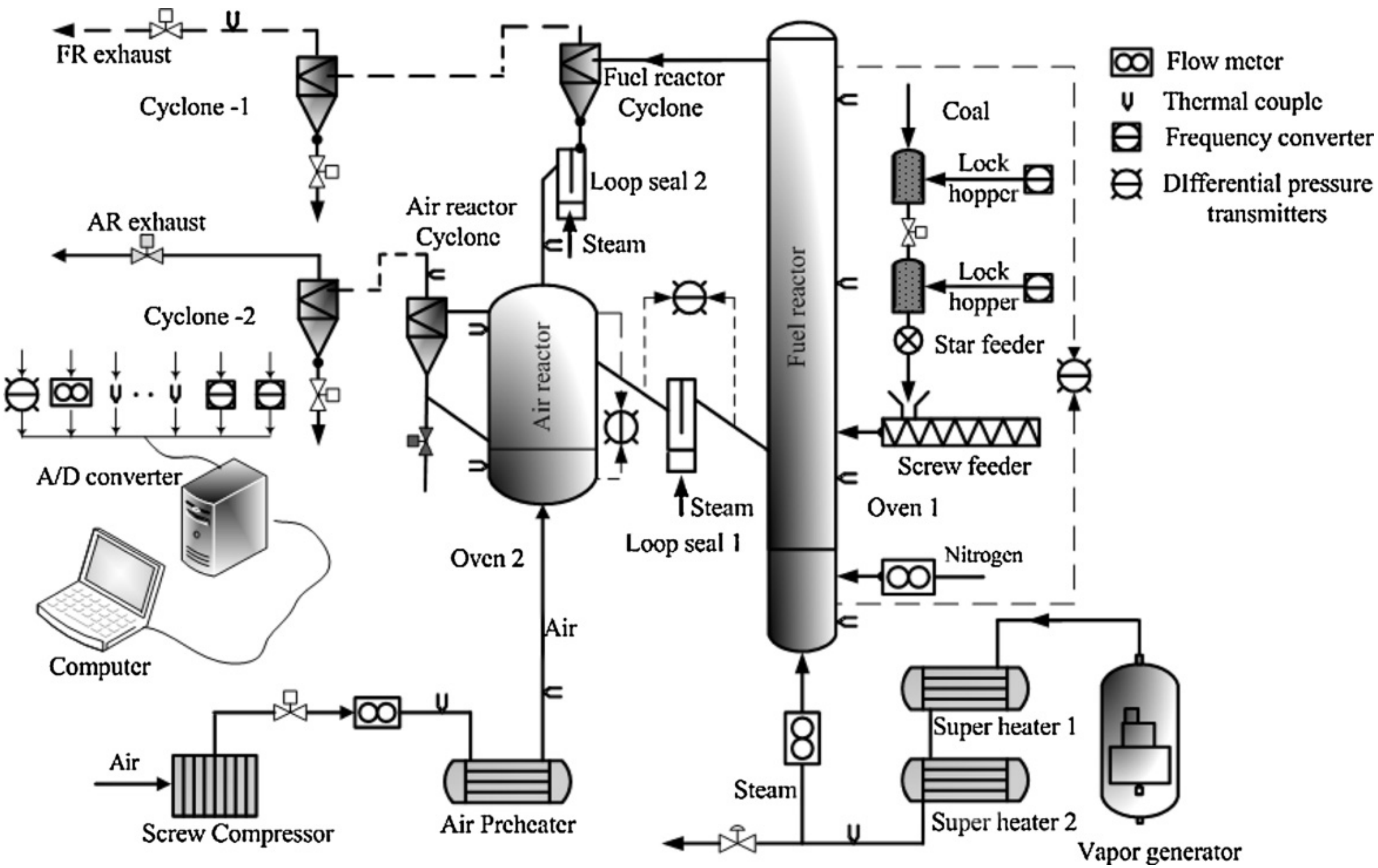


Ohio, 25 kW moving bed CLC, 2012

- Coal fed in middle of moving bed

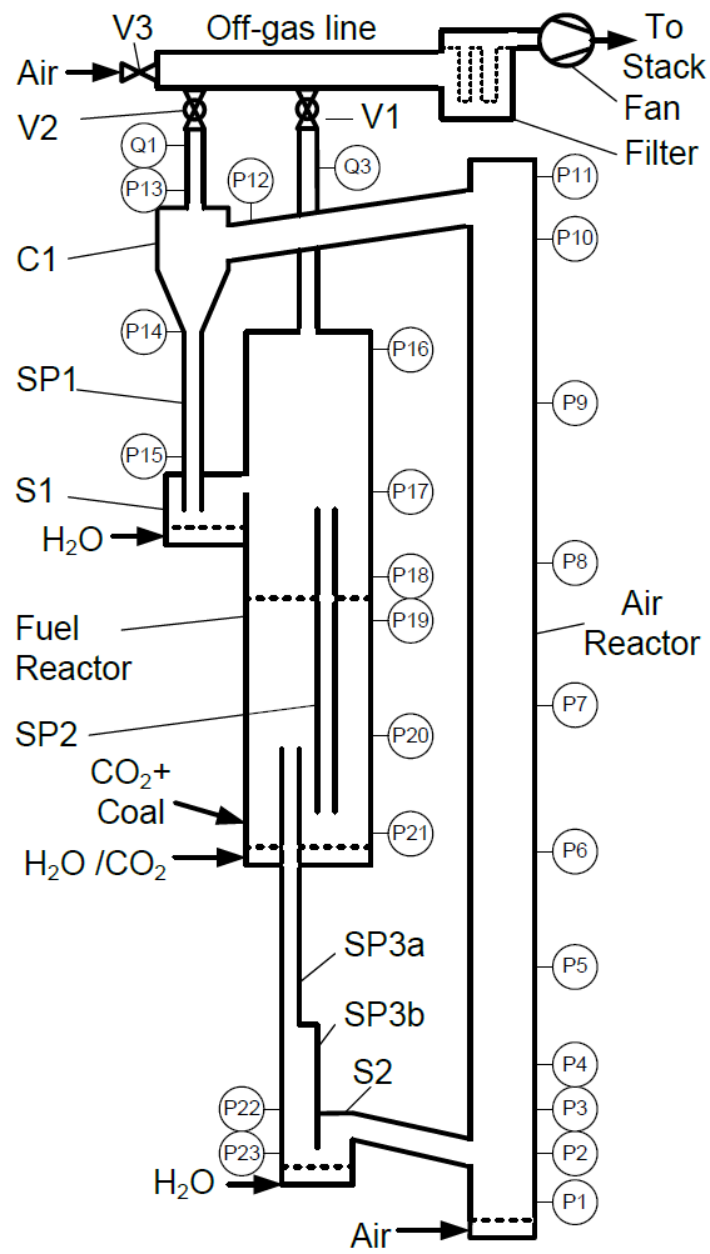


50 kW pressurized CLC, Nanjing 2012



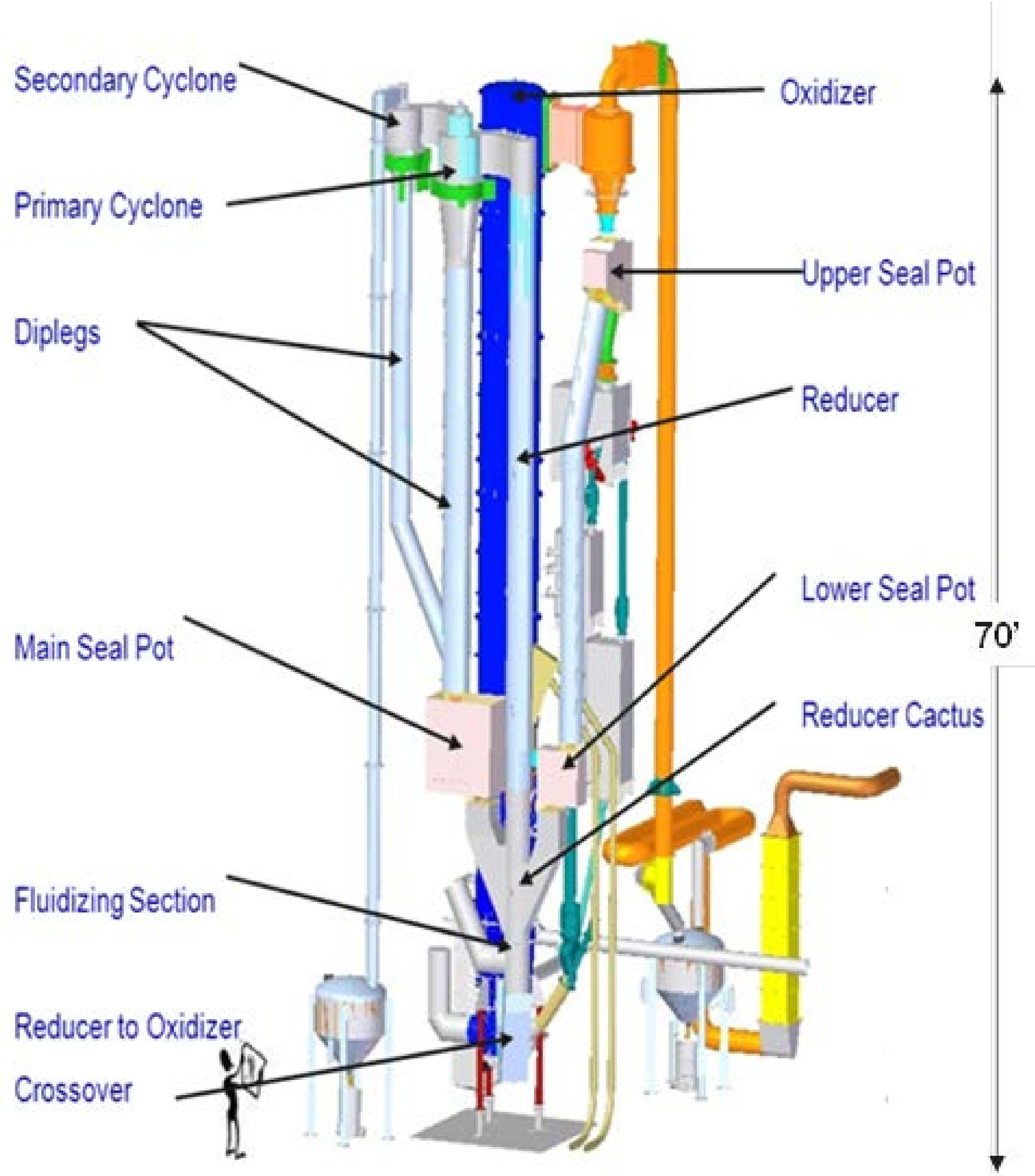
Hamburg 25 kW CLC, 2012

- 2 fuel reactors on top of each other
- coal fed in lower bed



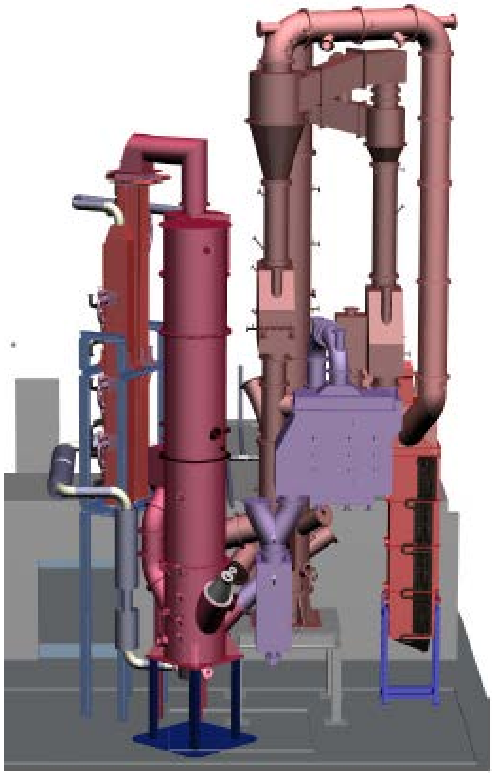
Alstom 3 MW

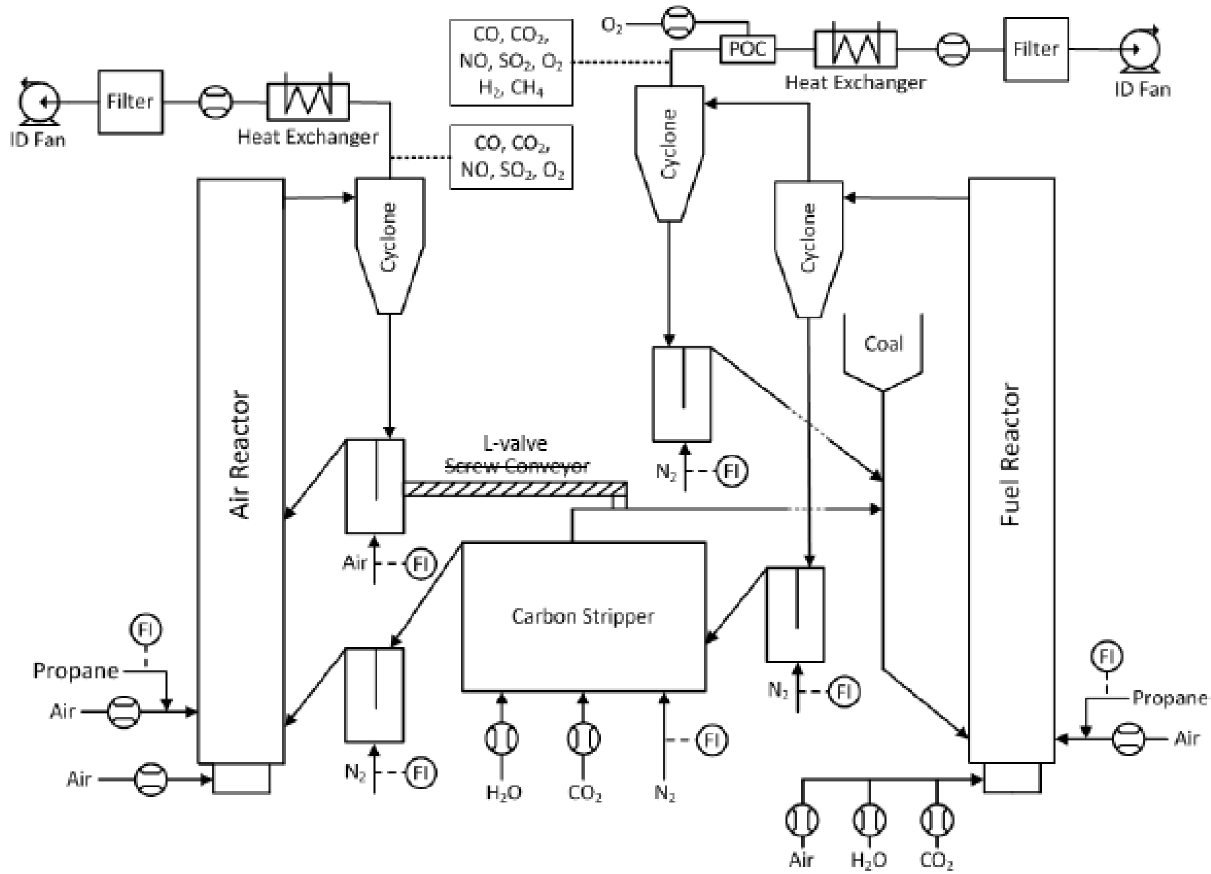
- High velocities
- $CaSO_4$ – CaS
- 2014



$1MW_{th}$ CLC in Darmstadt, 2014

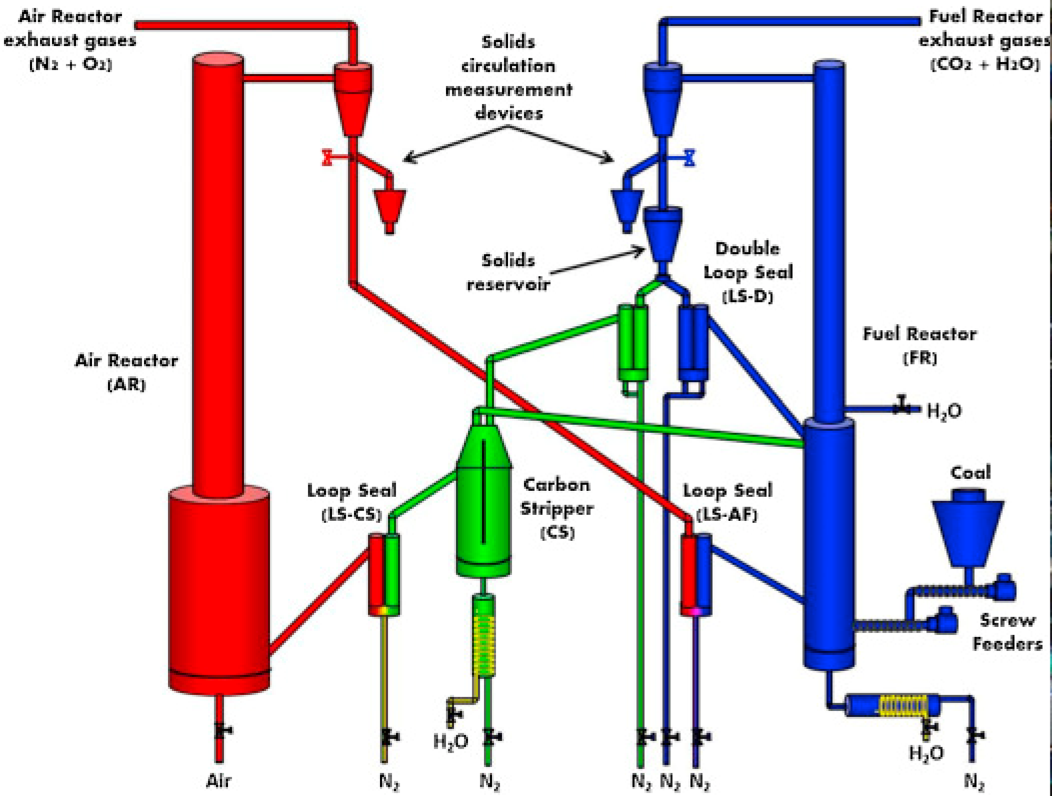
Autothermal operation (publ. 2016)





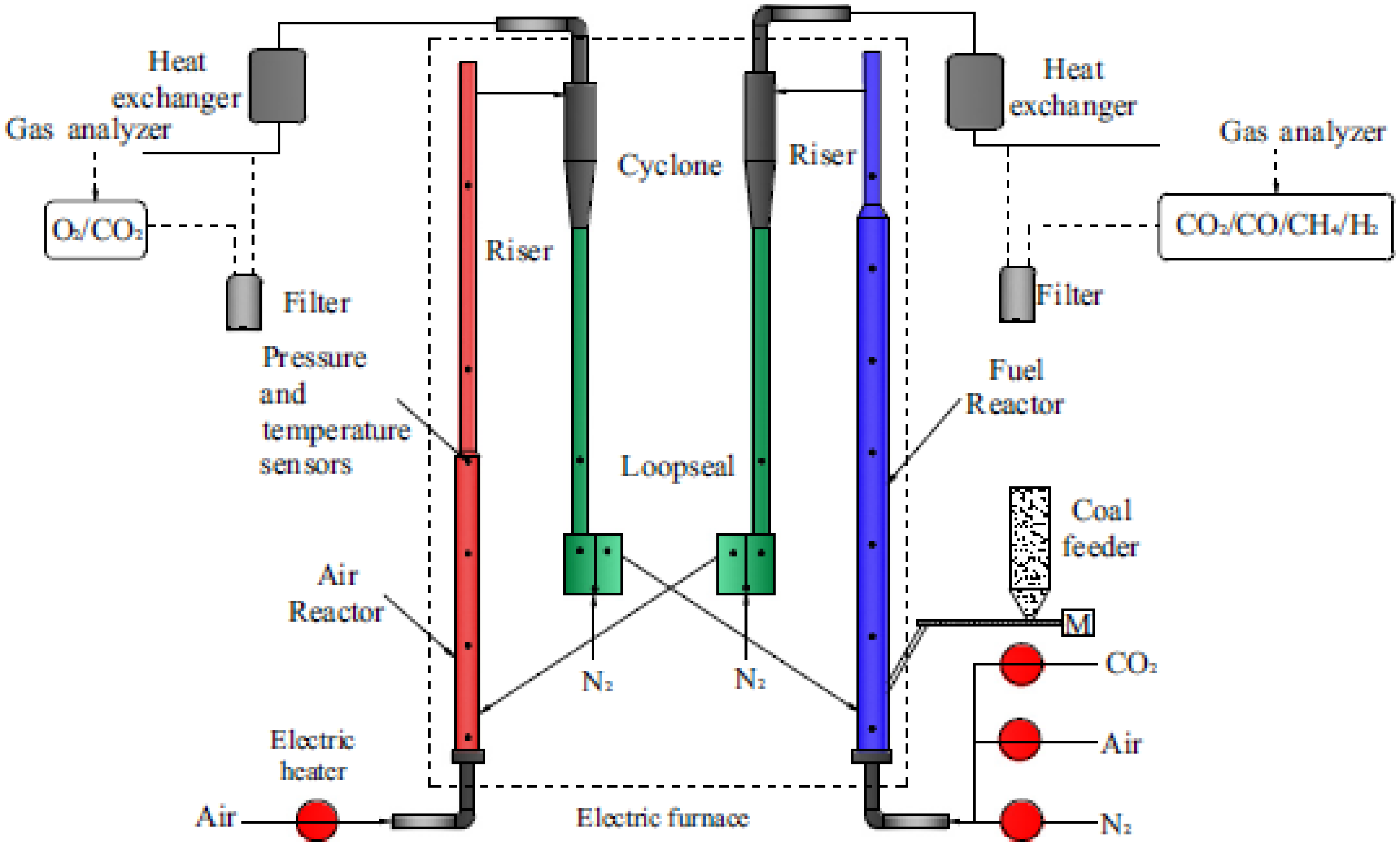
CSIC 50 kW CLC, 2014

- double loop seal
- operation at 13 kW
- high performance

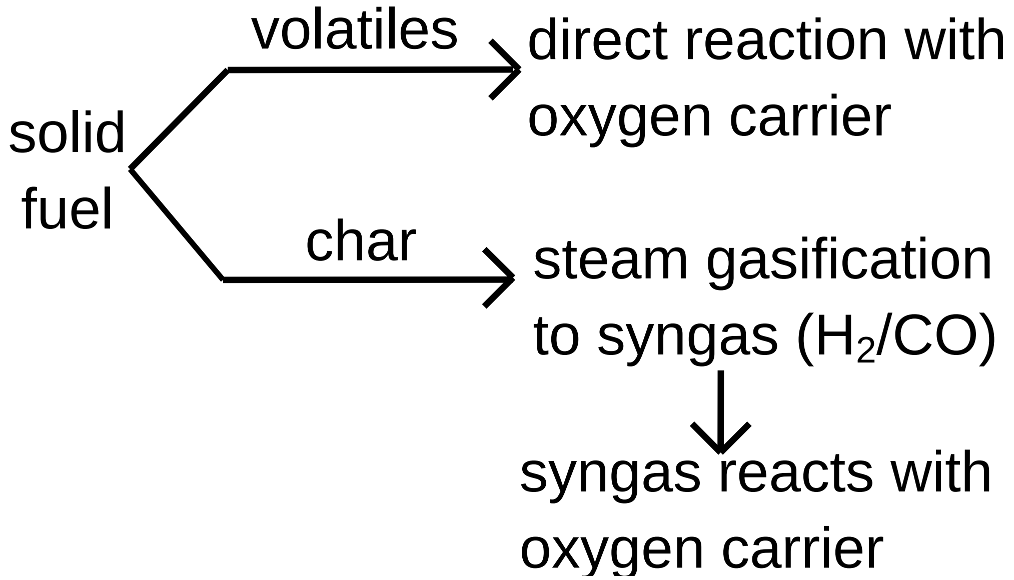


Huazhong 5 kW CLC, 2015

- two interconnected circulating fluidized beds

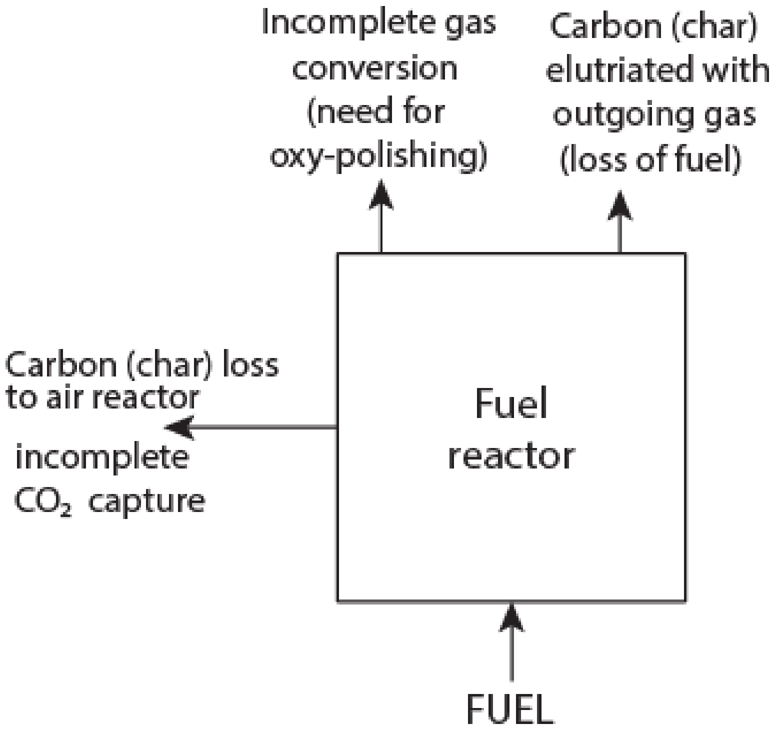


Operation with solid fuels



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.



$\Rightarrow$ 3 performance criteria:
$\Rightarrow$ 1) oxygen demand
$\Rightarrow$ 2) carbon loss
$\Rightarrow$ 3) CO_2 capture

1) Oxygen demand

- Reactivity oxygen carrier
  - Most reactive mtrls, too expensive or poor lifetime

- CLOU
  - Best CLOU mtrl (copper) expensive
  - $CaMnO_3$ less costly but sensitive to sulphur

- Gas-solids contact
  - High for gas from gasification
  - Poor for volatiles
  - Bottom bed: reduces with increasing velocity
  - Riser: increases with increasing velocity and height

- Solids inventory
  - Gas-solids contact decreases with increasing height

2) Carbon loss

- Char reactivity
  - Choice of fuel
- H_2O concentration
  - Expensive to add extra H_2O to fuel reactor
- Temperature
  - Very strong temperature dependence, T>980 C suitable in fuel reactor
- Residence time
  - Cyclone efficiency for recirculation of char fines
  - Riser height, significant difference between 4 m pilot and 50 m full scale
- Fuel size
  - Avoid fines, e.g. pulverized coal
  - 100-300 mm coal likely optimal

3) CO_2 capture

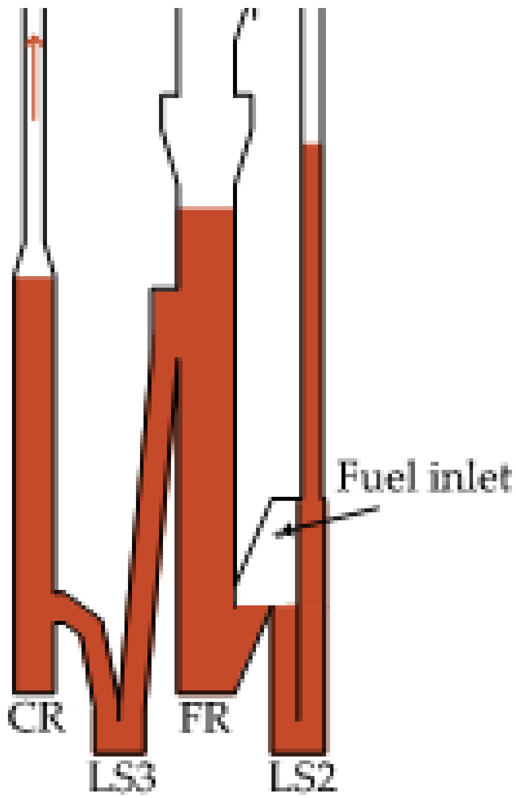
- As with carbon loss:
  - Reactivity, choice of fuel
  - H_2O concentration
  - Temperature

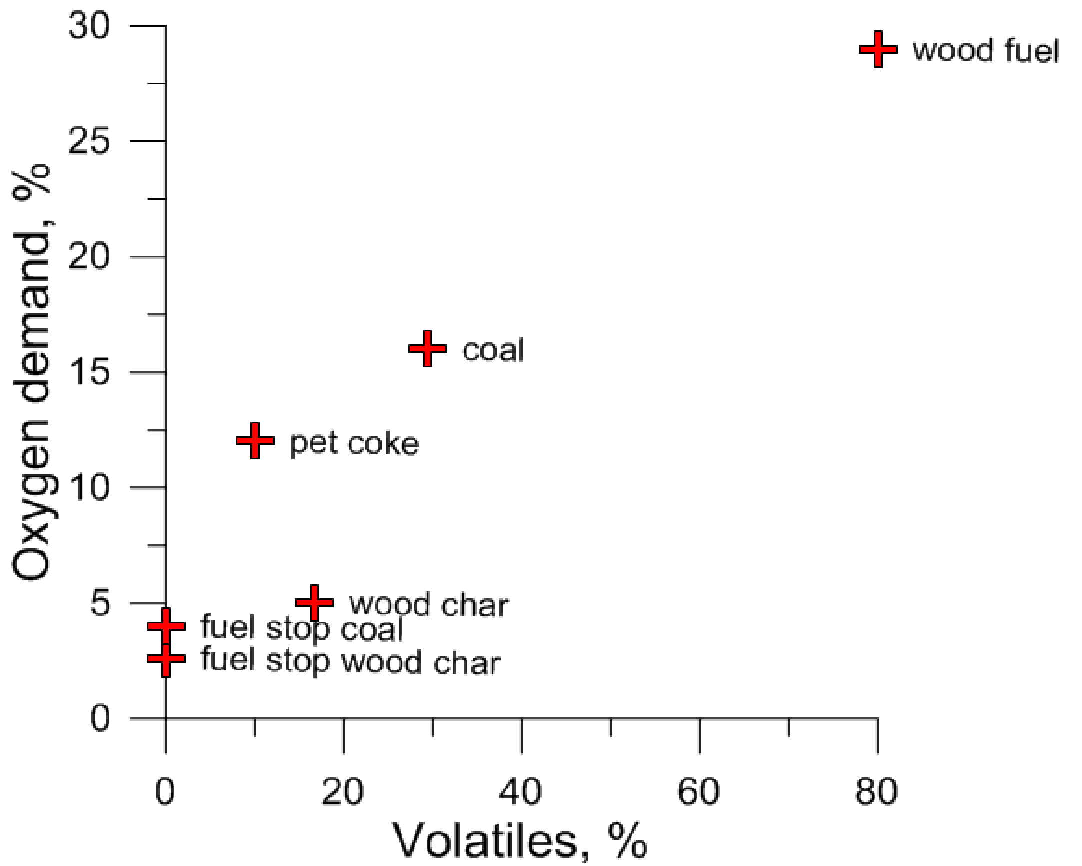
- Residence time (different from carbon loss)
  - Solids inventory
  - Carbon stripper

- Fuel size
  - Avoid large particles
  - 100-300 mm coal likely optimal (cf. carbon loss)

PILOT CLC OPERATION

Much higher conversion with low-volatile fuel (100 kW)





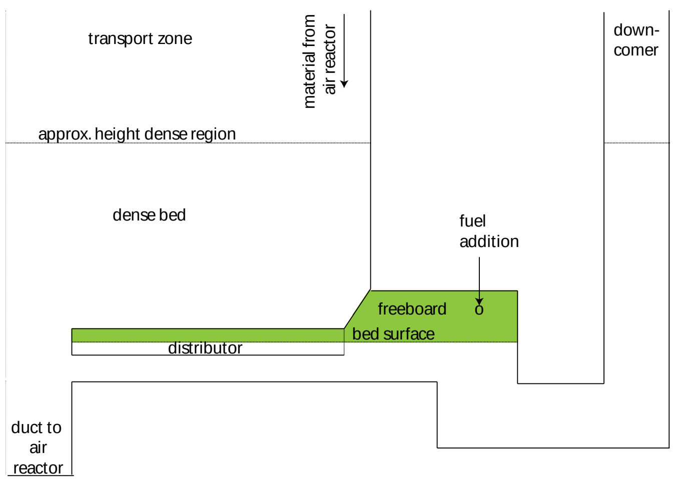
Likely reasons for good conversion of syngas from char / bad conversion of volatiles:

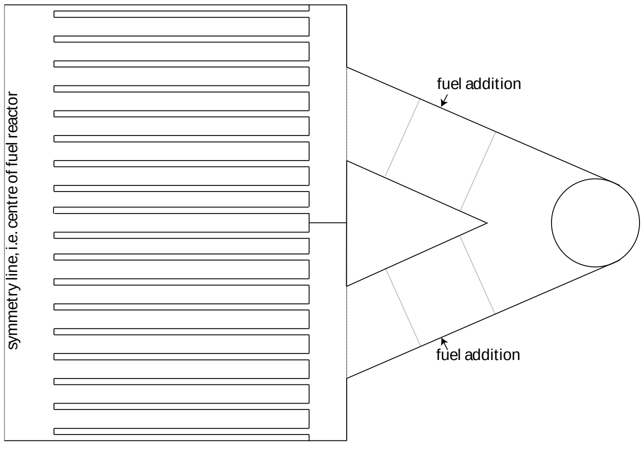
Rapid devolatilisation gives volatiles in bubble phase. Bubbles by-pass the bed, limited contact with bed material

Char particles mixes into dense phase, where there is intimate contact between oxygen carrier and syngas released by gasification.

What is the effect of scale-up ?

Risk of volatiles concentrating above fuel feed. System for volatiles distribution proposed.[1]





[1]Lyngfelt, A., and Leckner, B., A 1000 MW_{th} Boiler for Chemical-Looping Combustion of Solid Fuels - Discussion of Design and Costs, *Applied Energy* **157** (2015) 475-487

Poor CO_2 capture with large coal particles

	3 MW Alstom	1 MW Darmstadt, ilmenite		100 kW at Chalmers			50 kW, CSIC
	coal $CaSO_4$ [63]	PC [55][1]	LC [56]	PC, ilm [48]	PC, ilm + Mn ore 1 [50]	IC, Mn ore 2 [60]	IC, ilm, test 6 [54]
Carbon capture, η_{CO2}, [%]	96	80	44-52	98-99	99	99	90
Carbon loss by elutriation, $1-\eta_F$ [%]	0.5	50	5	35	(26-46)	**8-12**	**7**
Oxygen demand, Ω_{OD}, [%]		20[1] (26-38)	22-28	17-25	**8,5**-18	11-17	10
Pressure drop fuel reactor, kPa			7.5	14-25			9
Solids inventory, kg/MW		156	105	300-500[2]			480
T FR, °C		900	920-950	965-980	960-974	970-980	990

[1] Not isothermal. Propane and air added to fuel reactor to keep up temperature. [2]fuel reactor, PC = pulverized coal: a majority below 90 µm, LC = larger coal, <8 mm, IC = intermediate sized coal: a majority in the size range 90-300 µm.

High CO_2 capture possible

High carbon loss with pulverized coal

Reasonably low oxygen demand

CONFLICT :
Large particles - poor CO2 capture
Small particles - large carbon loss

SOLUTION:
Intermediate size particles
100-300 microns

PC = pulverized coal, LC = large coal (<8 mm), IC = intermediate size coal (90-300 µm)

Scale-up discussion

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

High riser, high velocity and high cyclone efficiency recommended

- to raise residence time to fines, i.e. low loss of carbon
- to give good gas contact, i.e. low oxygen demand

Scale-up

High temperature

- Needed for high CO2 capture and low carbon loss
  - Strong temperature dependence, T>980 C recommended in FR

Low-cost materials likely optimal

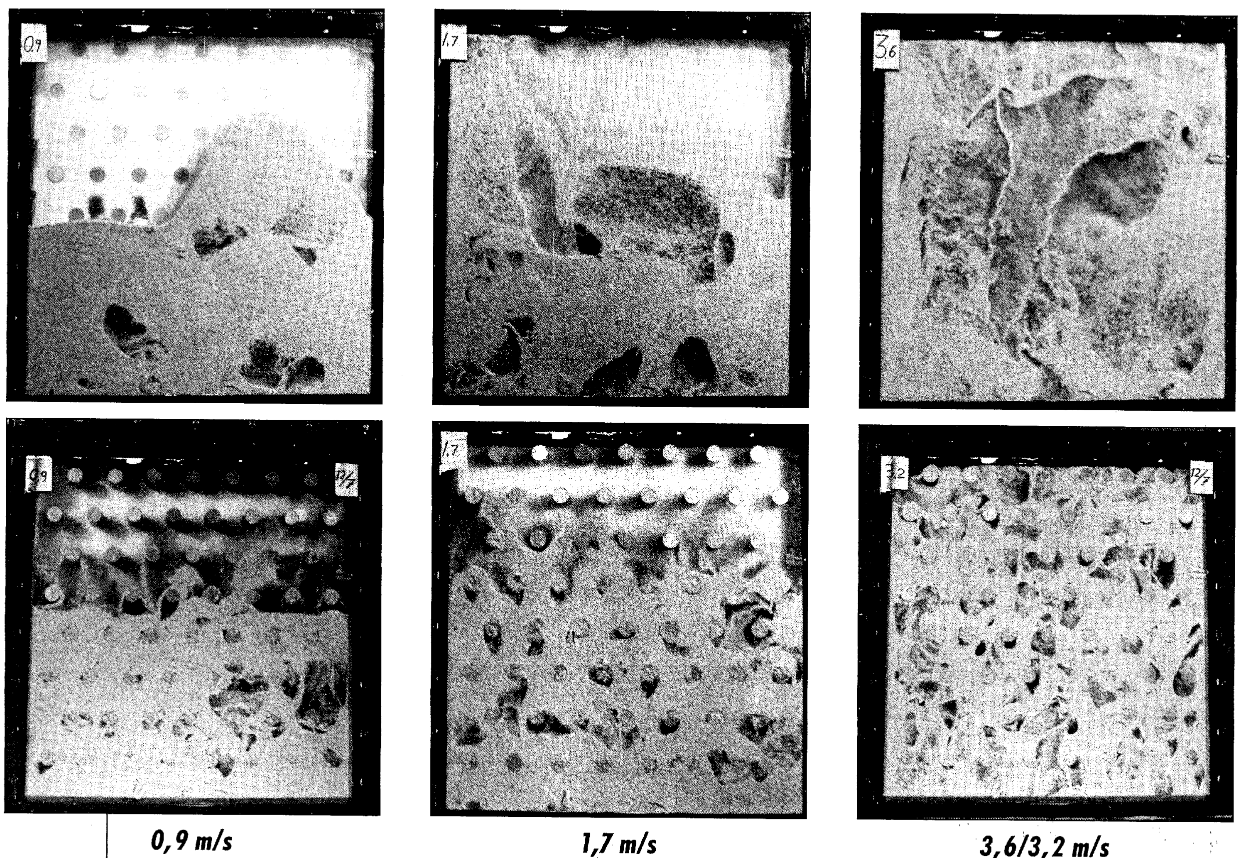
Incomplete conversion difficult to avoid

- Downstream oxygen polishing likely best way to reach full conversion

Scale-up

Gas-solids contact

- Fuel feed in bottom of bed
- Measures to improve contact need investigation:
  - Bed internals
  - Volatiles distributor (to accomodate for large cross-section)



Without internals

With internals

Scale-up

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

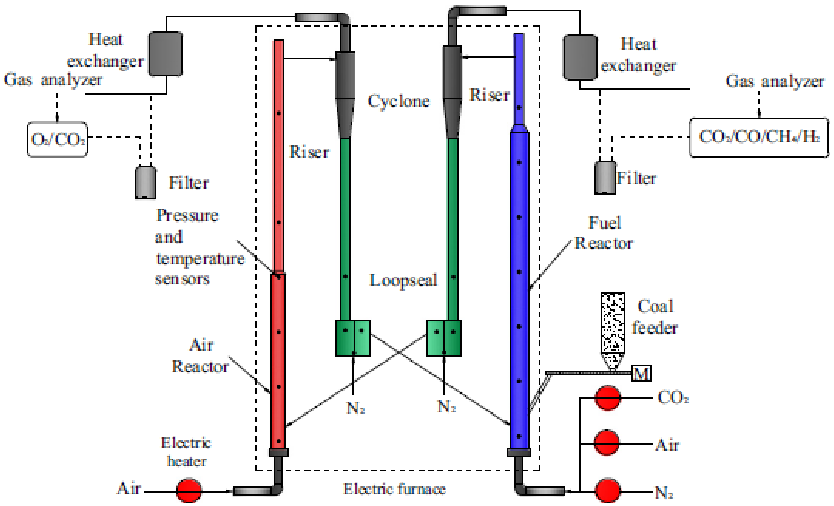
High solids inventory

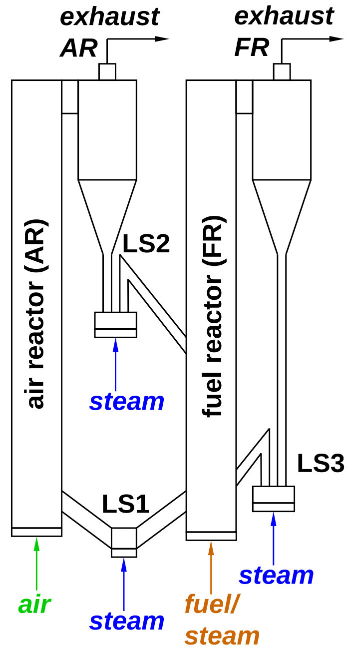
- Residence time needed to convert char particles
  - Additional residence time for char conversion in carbon stripper
  - How much can bottom bed height be increased ?

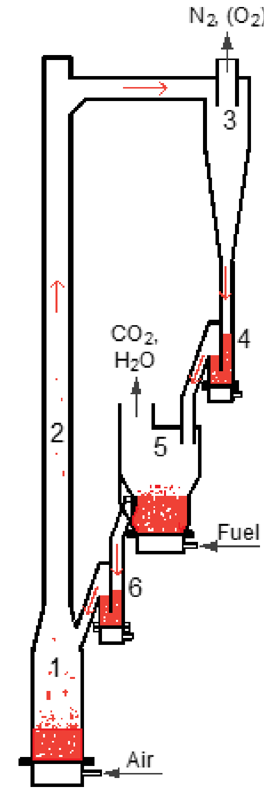
Scale-up, key challenge

- Circulation control
  - It is ***absolutely necessary*** to have an excellent control of circulation
    - Loss in circulation stops conversion within a minute
    - Circulation must be right
      - if too low, loss in fuel reactor temperature
      - if too high, loss in CO_2 capture
  - A number of different systems have been tried, and works well, in small pilot scale

Scale-up, circulation systems







Double control, i.e. control of flows from both air and fuel reactors

- Advantage, possibility to control solids inventory independently
- Risk, if flows are not exactly equal, one reactor will empty rapidly

Hydraulic connection between air and fuel reactors

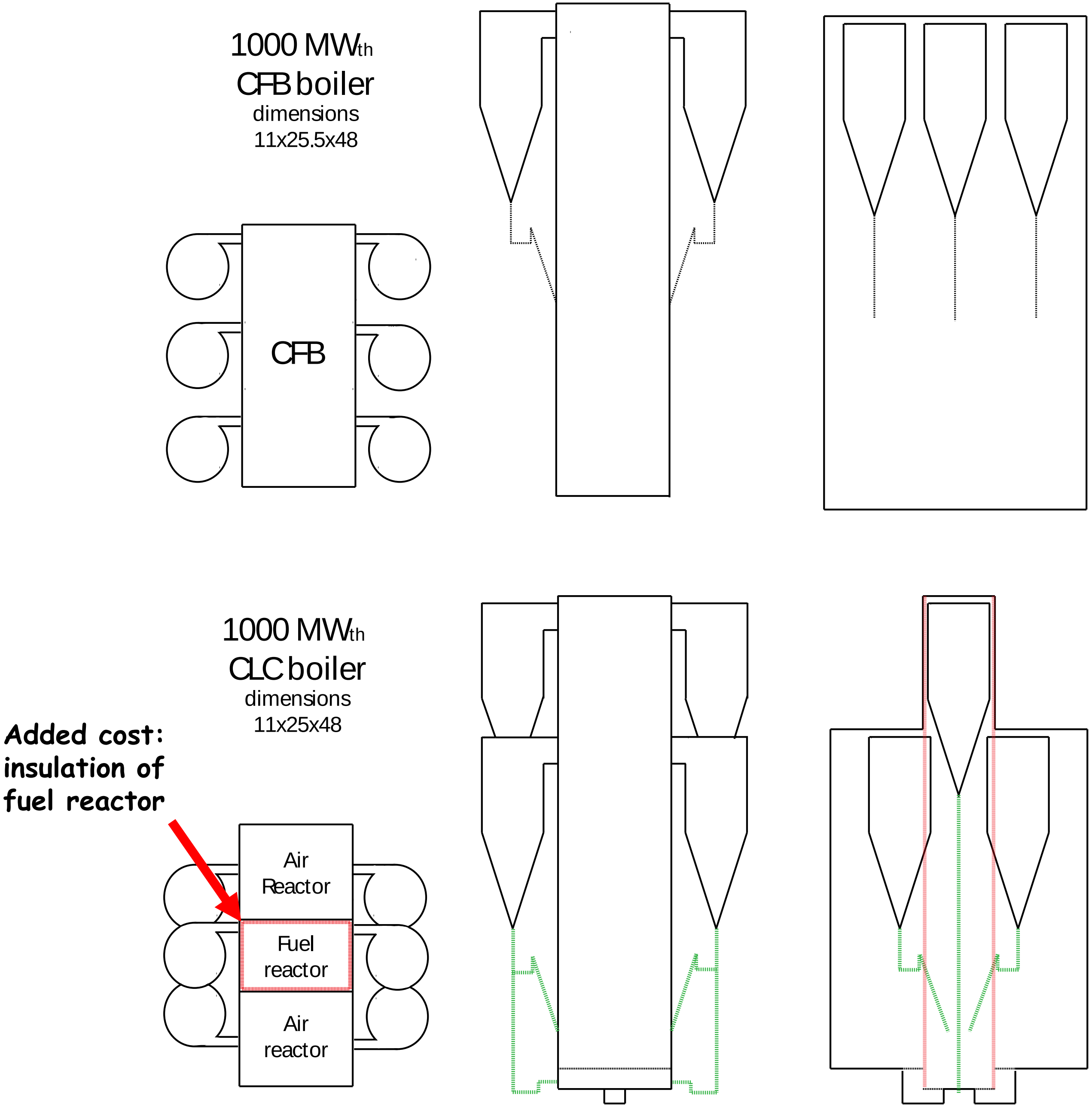
- Safe way of assuring presence of material in both reactors
- Not possible to increase solids inventory in only one reactor

:

Overflow exit from fuel reactor

- Safe way of assuring presence of material in fuel reactor
- Control of material in air reactor by addition/removal of material
- Solids inventory in fuel reactor may be changed by modifying overflow (turn-down needed)

- System for circulation control
  - Gas velocity in air reactor (rapid response)
    - Change gas flow
    - Play with primary/secondary air
  - Particle size, main control option (slow response)
  - Split loop-seal (large-scale application risky in my mind)
  - Additional riser with higher velocity dedicated for controlling circulation



Fuel reactor, cyclones, ducts and post-oxidation chamber: 2500 m²

Cost: 1500 €/m²

Added cost of fuel reactor:

4 M€

0.4 M€/year
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)*

Added cost relative to CFB[1]

Type of cost	estimation, €/tonne CO_2	range, €/tonne CO_2	Efficiency penalty, %
CO_2 compression	10	10	3
Oxy-polishing	6.5	4-9	0.5
Boiler cost	1	0.1-2.3	-
Oxygen carrier	2	1.3-4	-
Steam and hot CO_2 fluidization	0.8	0.8	0.8
Fuel grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
Total	20	15.9-25.8	3.9

Scale-up, first step without CO_2 capture, to assess technology

- Main costs: Downstream treatment and oxygen production not needed
- CO_2 capture could be added afterwards
- or, with suitable design, system can be used as CFB afterwards (dual purpose)

Type of cost	estimation, €/tonne CO_2	range, €/tonne CO_2	Efficiency penalty, %
~~CO_2 compression~~	~~10~~	~~10~~	~~3~~
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Steam and hot CO_2 fluidization	0.8	0.8	0.8
Fuel grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
Total	3.5	1.9-6.8	0.4

[1] Lyngfelt, A., and Leckner, B., A 1000 MW_{th} Boiler for Chemical-Looping Combustion of Solid Fuels - Discussion of Design and Costs, *Applied Energy* **157** (2015) 475-487

Scale-up – final remarks

Fuel size:

- Use intermediate size, 90-300 μm
  - High CO_2 capture and low loss of char

Reactor and system design:

- Use existing proven CFB technology when possible

Scale-up strategy, lower cost by

- First step without CO_2 capture
- Dual purpose unit, i.e. CLC that can be used as CFB.

Circulation system/control

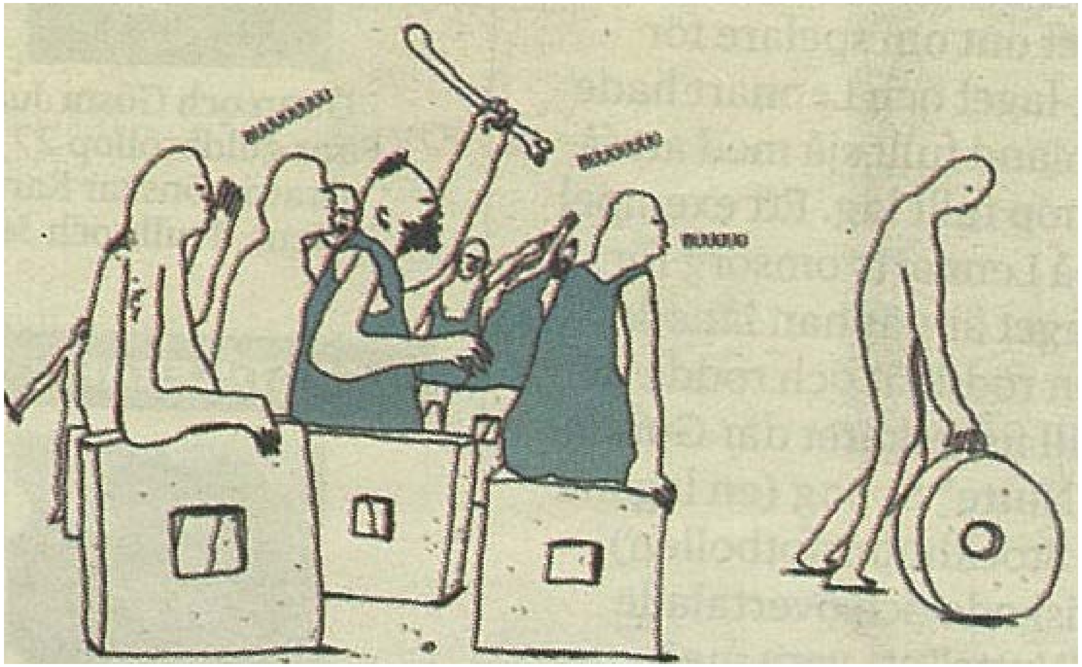
- Key for successful operation

Pilot operation:

- >8000 h of operation and ~3000 h with low-cost mtrls shows CLC is feasible.
  - More work on low-cost mtrls, *e.g.* Mn ores, would be valuable
- **BUT, additional small-scale pilot operation will *not* answer key questions related to performance in full-scale**
  - Small pilots do not have relevant height to show conversion possible in full-scale riser, wrt. conversion of gas and char
  - High bottom beds possible, but will be slugging because of high ratio H/D
- *Technology ready for scale-up !*

Right answer to *"What is needed to reach to reach full scale ?"* **is:**

Start the up-scaling!



Is CLC a break-through technology for CO_2 capture?

☒ **Yes**

THANK YOU !!!
QUESTIONS

>290 publications on CLC to be found on:

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