Oxygen-Carriers for Chemical-Looping Combustion - Operational Experience

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Contents

Brief history

Different applications

Testing in chemical-looping combustors

1946/1954 Patent by Gilliland :

"Production of industrial gas comprising carbon monoxide and hydrogen"

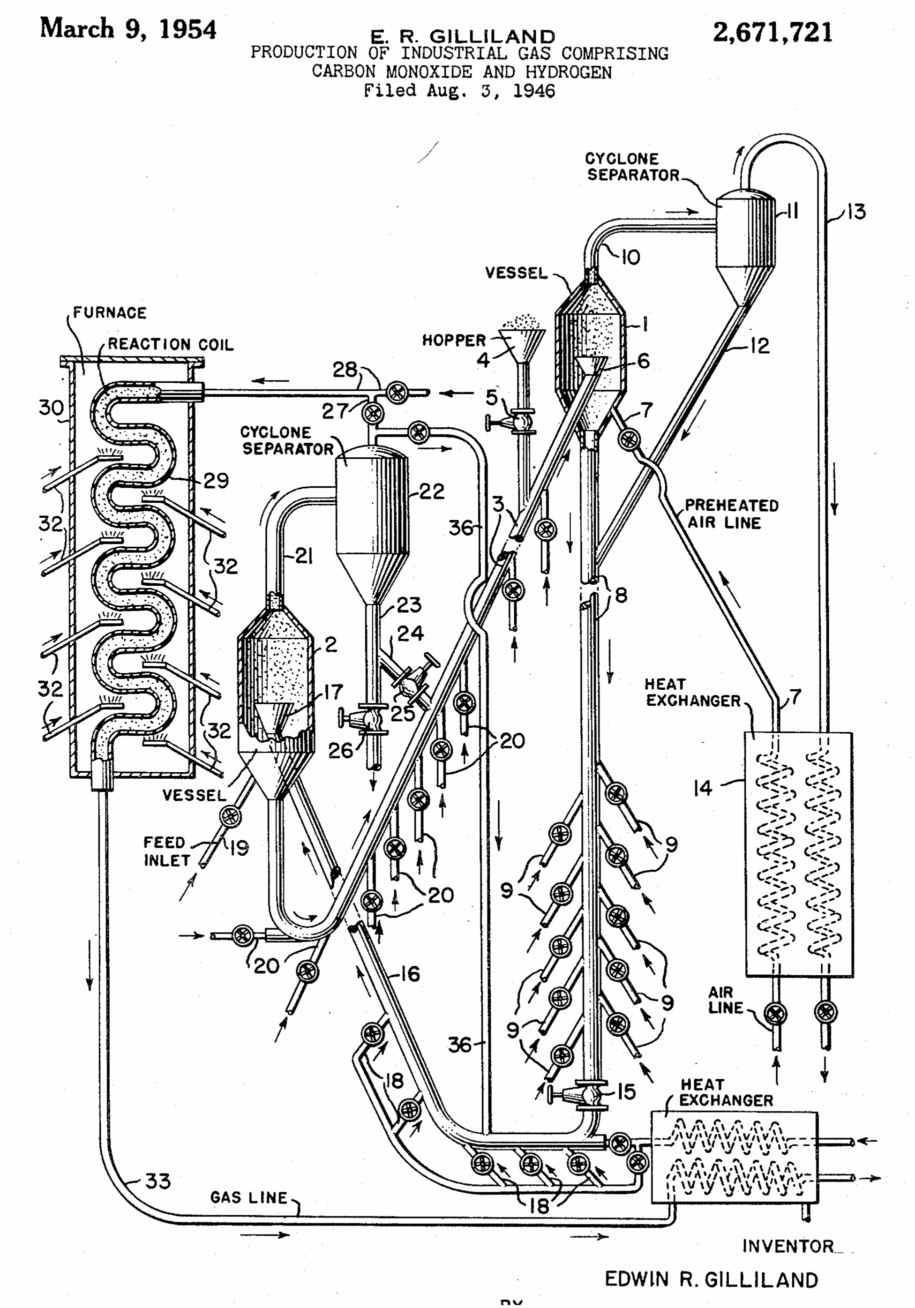
"a metal as oxygen carrier, … first reacted with air to produce an oxide, then … reacted with the hydrocarbon to … carbon monoxide and hydrogen" "finely divided metal oxide … in a fluidized state"

1950/1954 Patent by Lewis and Gilliland :

"Production of pure carbon dioxide"

using a "solid oxygen carrier" using "any oxidizable carbonaceous material", such as charcoal, coal, coke.... natural gas.... lignite... using two interconnected fluidized beds

From patent by Gilliland filed 1946



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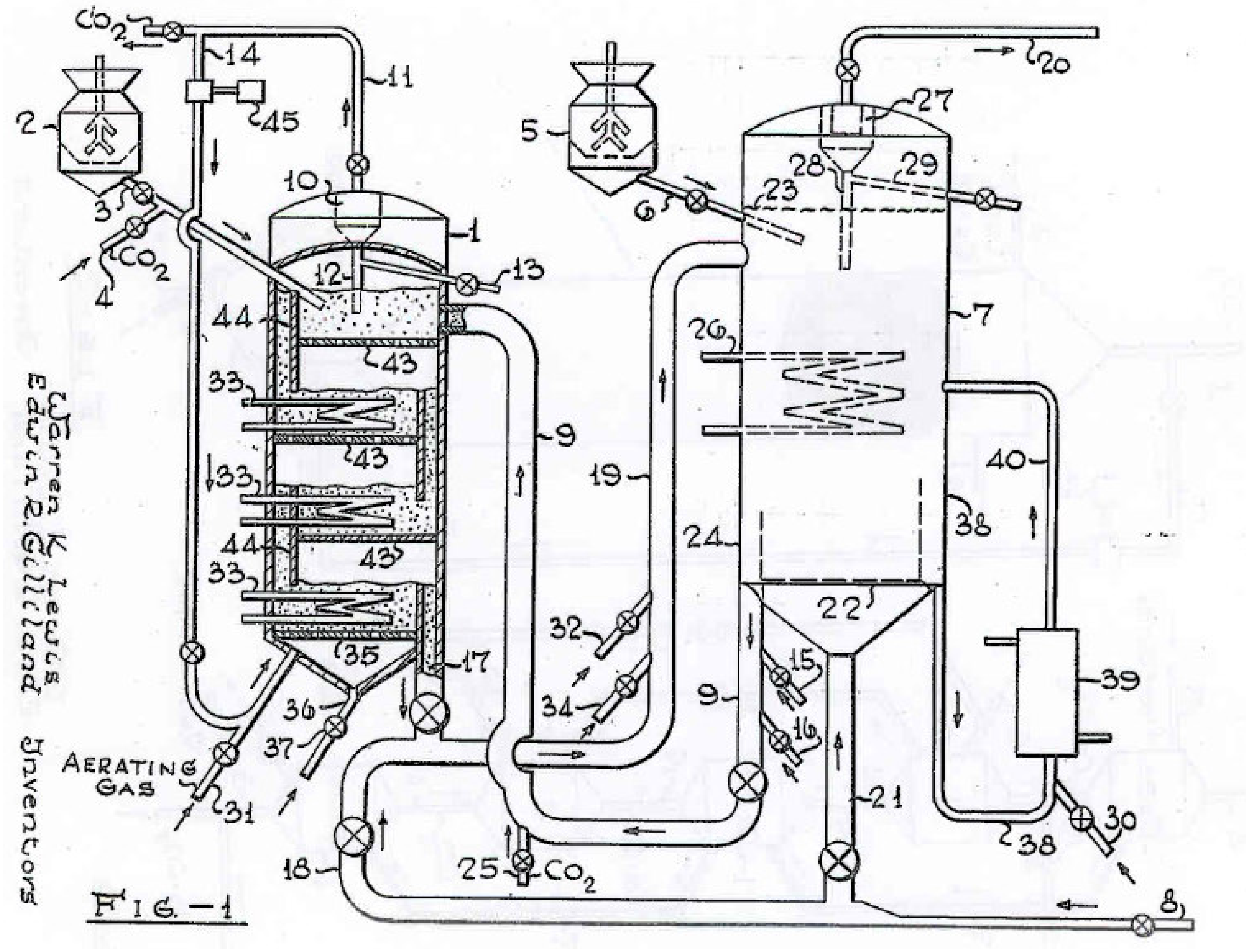


From patent of Lewis & Gilliland filed 1950

1983 Thermodynamic study by Richter & Knoche:

"Reversibility of Combustion Processes" proposing the principle of CLC to increase efficiency

1987 Thermodynamic study by Ishida introduces the name "*Chemical-Looping Combustion*"

1988 experimental study by Ishida on Fe_2O_3, followed by a number of papers in the 90'ties on Fe-, Ni

1994 Ishida proposes the use of CLC for *CO_2 capture*

1980-1995

1997 Hatano presents exp. data for new concept "MERIT" (mediator recycling integrating technology)

1998 Yours Truly *goes* totally looping, after a visit from Japan at Chalmers

1999/2000 Lyon proposes "Unmixed reforming" for natural gas / "Unmixed combustion" for solid fuels, including experimental data

2000 Copeland presents "Novel CO_2 separation system" later named SETS (sorbent energy transfer system)

1995-2000

2001 GE EER proposes process for production of H_2 from coal

2001 Lyngfelt proposes 10 MW reactor design based on exp. data

2003 >100 h of operation in 10 kW unit at Chalmers

2003 ENI proposal of "one-step hydrogen" with water-splitting

2005 Patent application by Chalmers for CLOU (Chemical-Looping with Oxygen Uncoupling), CuO decomposition already noted by Lewis & Gilliland

2000-2005

2006 first operation with CuO > 100 h, CSIC

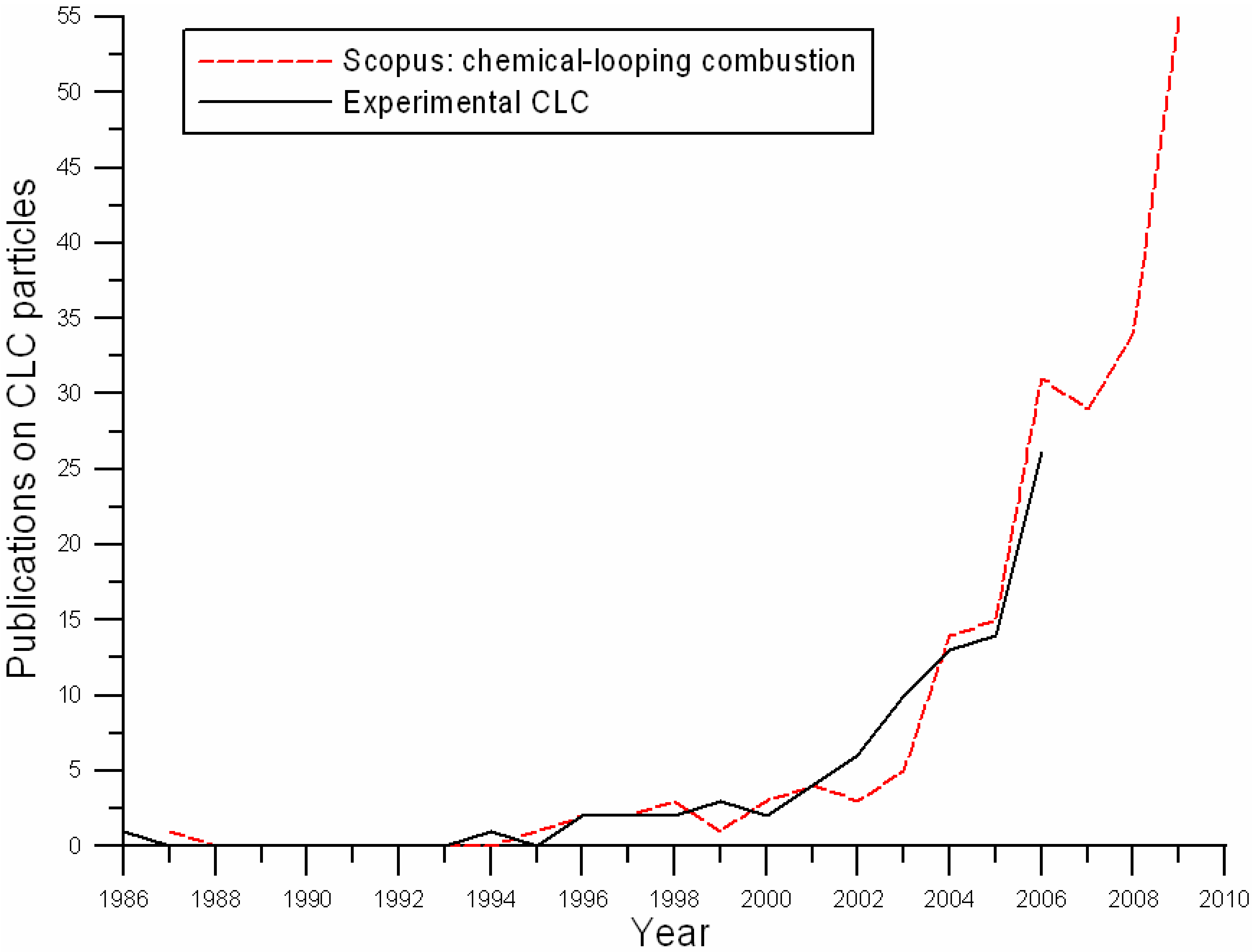
2006 Rydén proposes "Chemical-Looping Steam Reforming"

2006 solid fuel CLC in continuous operation, Chalmers

2008 120 kW dual CFB operated in Vienna

2010 *1st International Conference on Chemical-Looping*, in Lyon

2010-



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Chemical-looping steam reforming:

Marriage between conventional steam reforming and chemical-looping atmospheric combustion

Natural gas at 18 €/MWh gives hydrogen fuel with no CO_2 at around 38 €/MWh

That is, a CO_2 free fuel at todays world market price of crude oil, one third of price of petrol.

Chemical-looping applications

application \ fuel	gas	solid	liquid
combustion			
syngas generation			
chemical-looping steam reforming			
pressurized CLC			
CLOU			
water splitting			

Needed:

- **portfolio** of oxygen carriers for different applications, and for safety of supply
- operational experience with oxygen carriers, for credibility

Chalmers 10 kW

Dimensions:

AR: Ø 15 cm, riser 8 cm, height 2.23 m

FR: Ø 15 cm

Type:

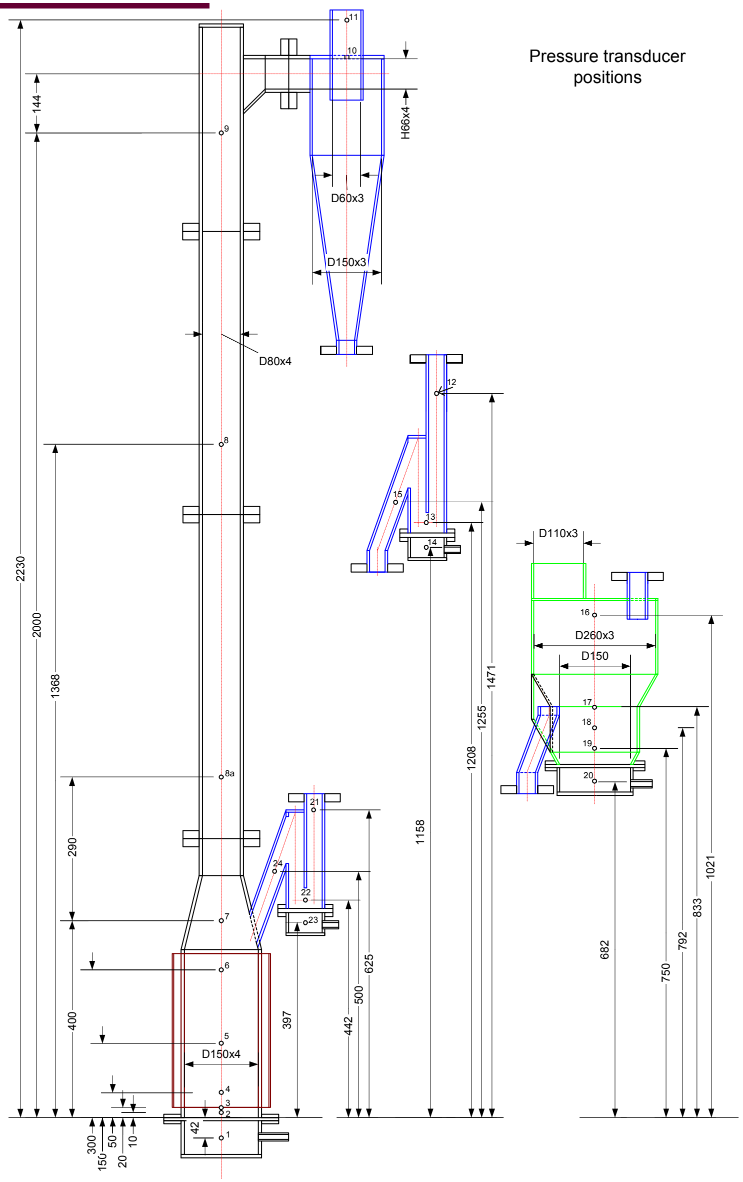
Circulating AR

Bubbling FR, with overflow

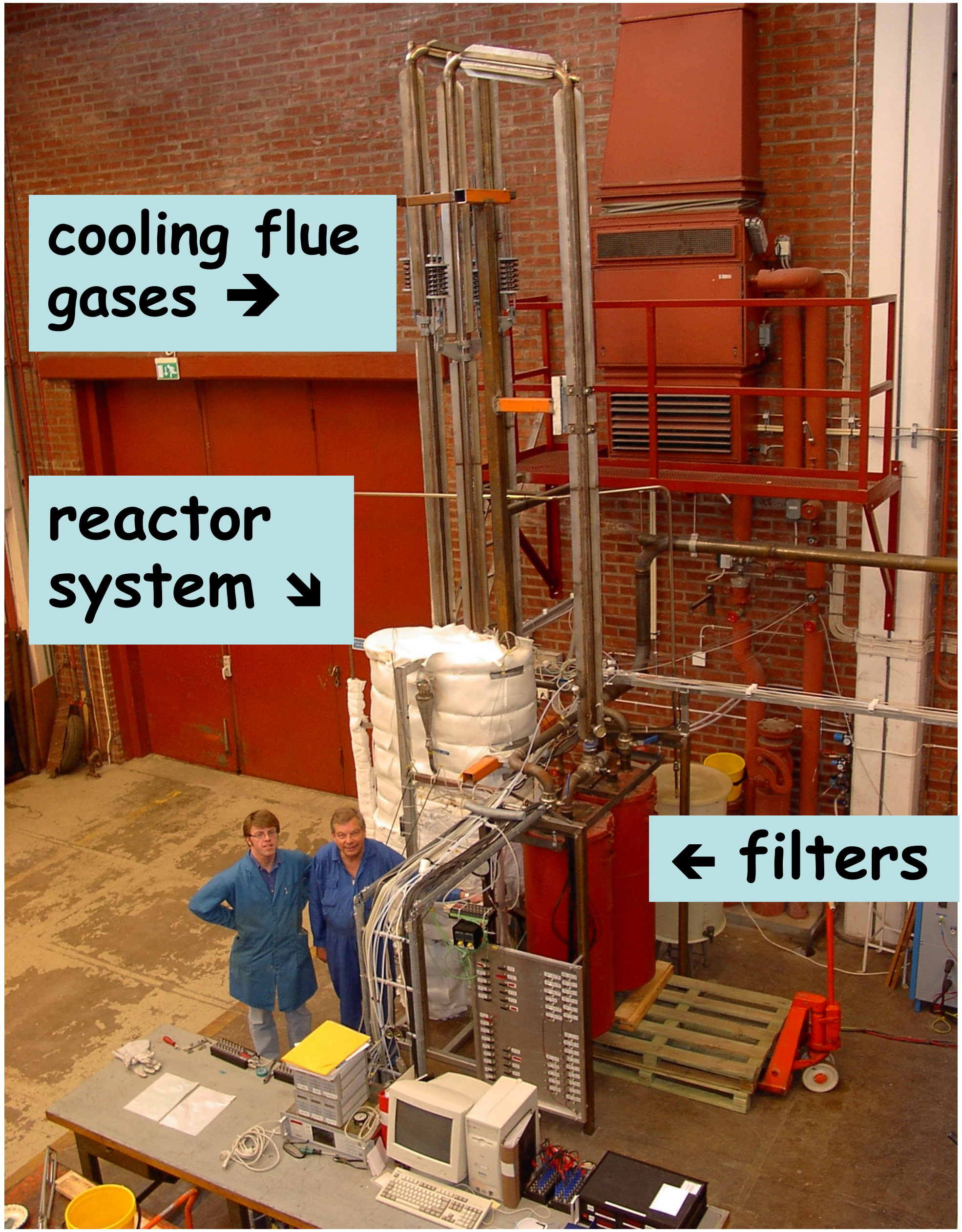
Two loop seals separating AR/FR

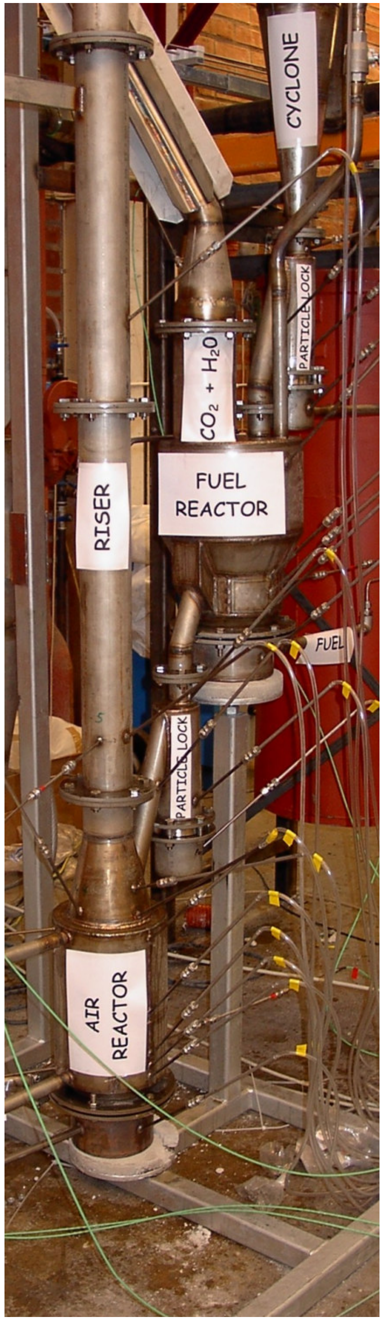
Fuel: natural gas

First published: 2004



Chalmers' 10 kW chemical-looping combustor 2003





Oxygen carriers:

- $NiO/NiAl_2O_4$ 40/60, freeze-granulated
- $Fe_2O_3/MgAl_2O_4$ 60/40, freeze-granulated
- $NiO/NiAl_2O_4$ 60/40, spin-flash drying
- NiO/Al_2O_3 18/82, impregnation
- $NiO/NiAl_2O_4$ 40/60, spray-dried
- $NiO/NiAl_2O_4/MgAl_2O_4$ 40/42/18, spray-dried

Total time of operation: 1355 h

Key results:

- no CO_2 from AR
- low attrition 0.002%/h
- high fuel conversion, 98-99%

Publications: 4

Korean Institute of Energy Research (KIER) 50 kW

Dimensions:

AR: Ø 10, riser 8 cm, height: 5 m

FR: Ø 14 cm, height 2.5 m

Type:

Circulating AR

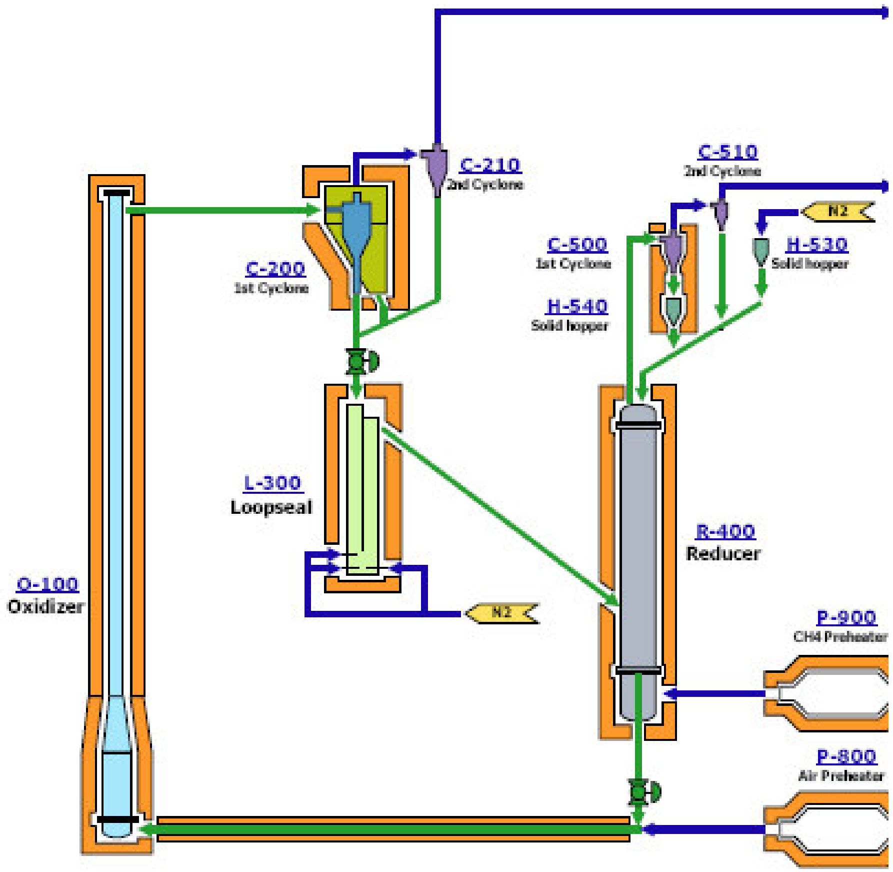
Bubbling FR, outflow via slide valve

Loop seal after AR

Slide valve + horizontal tube after FR

Fuel: methane

First published: 2004



Oxygen carriers:

NiO/bentonite 60/40, powders mixed/dried/crushed calcined

$Co_xO_y/CoAl_2O_4$ 70/30, co-precipitation/impregnation

Total time of operation: 3+25 h

Key results:

no gas leakage between reactors

no carbon formation

high fuel conversion, 98%

Publications: 2

CSIC-ICB Zaragoza 10 kW

Dimensions:

AR: Ø 16 cm, height 1.5 m

FR: Ø 10 cm, height 2 m

Type:

Bubbling AR, overflow exit

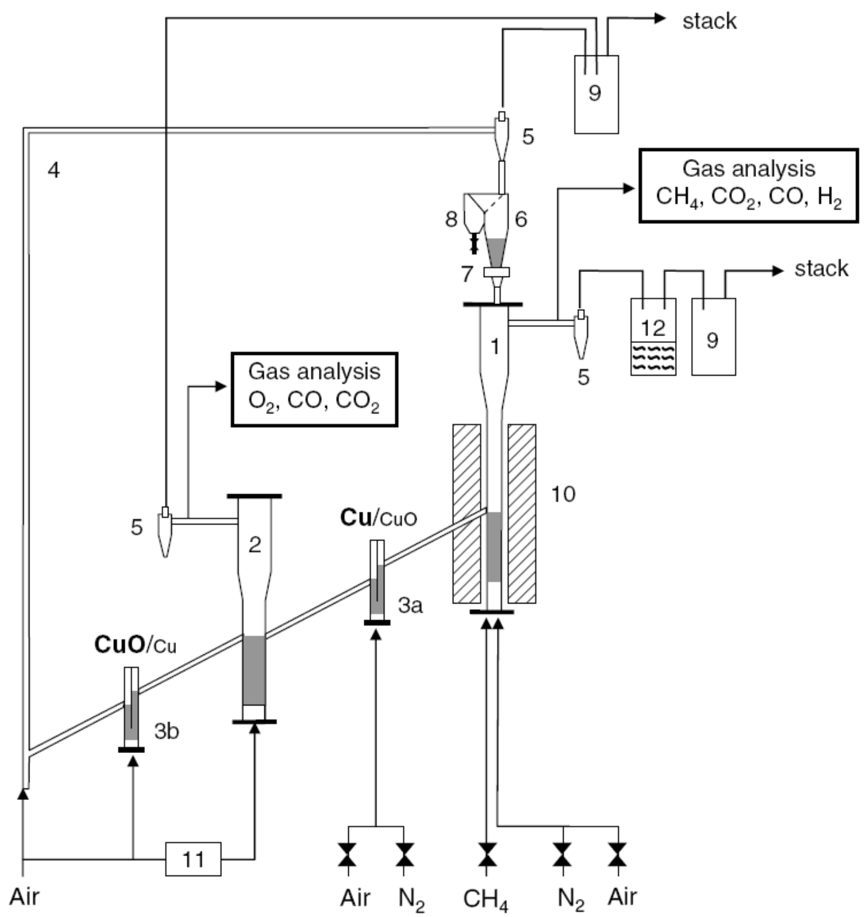
Bubbling FR, overflow exit

Loop seals after AR and FR

Overflow from AR led to separate air-blown riser, solids valve controlling flow to FR

Fuel: methane

First published: 2006



Oxygen carriers:

- **CuO/Al_2O_3 14/86, wet impregnation, 2 sizes**

Total time of operation: 120 h

Key results:

- **Complete conversion of CH_4 with CuO**
- **No gas leakage between reactors**
- **Long-term operation with CuO verified at 800 C**
- **CuO particles maintaining high reactivity**

Publications: 2

Chalmers 300 W, design 1/2

Dimensions:

- AR: 25x35 mm, 25x25 mm
- FR: 25x25 mm

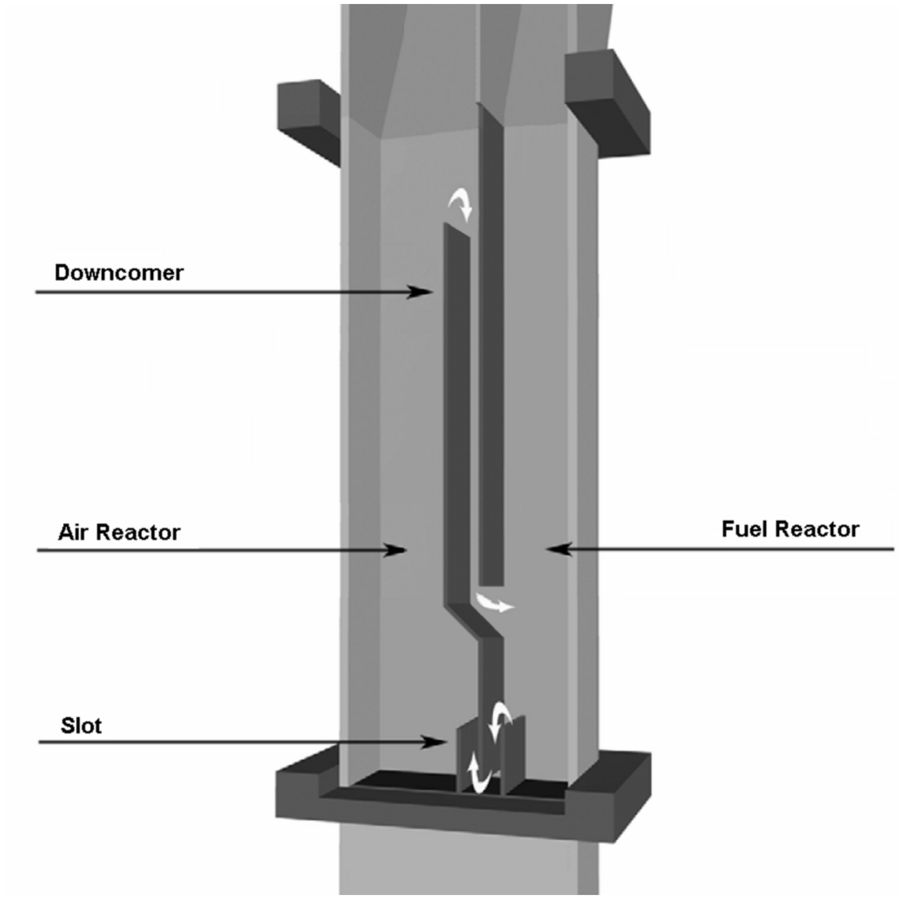
Type:

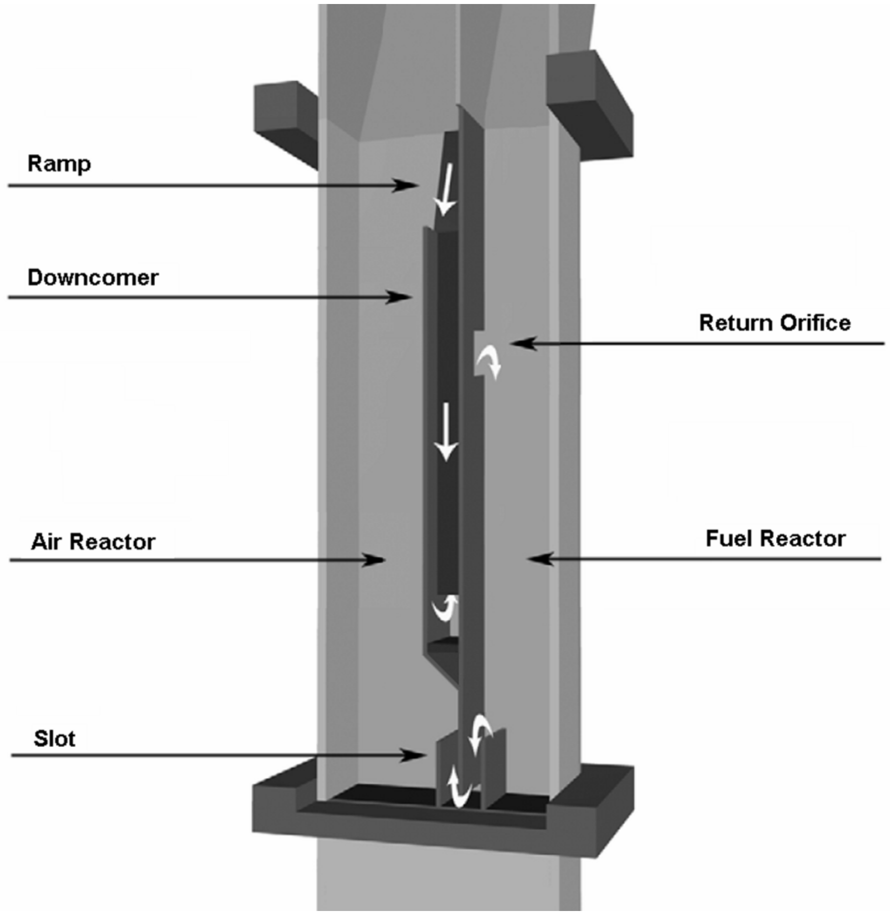
- Bubbling AR
- Bubbling FR, outflow via fluidized slot
- Particles thrown up from AR led through downcomer to FR

Design 2: Particle seal after AR, slot improved

Fuels: natural gas, CO/H_2

First published: 2006





Design 1

Design 2

Oxygen carriers:

- $NiO/MgAl_2O_4$ 60/40, freeze-granulated
- $NiO/NiAl_2O_4$ 40/60, freeze-granulated
- $Mn_3O_4/Mg\text{-}ZrO_2$ 40/60, freeze-granulated
- Fe_2O_3/Al_2O_3 60/40, freeze-granulated

Oxygen carrier (design 2):

- $NiO/MgAl_2O_4$ 20/80, freeze-granulated
- $NiO/\alpha\text{-}Al_2O_3$ 18/82, impregnation
- $NiO/\gamma\text{-}Al_2O_3$ 21/79, impregnation
- $Fe_2O_3/MgAl_2O_4$ 60/40, freeze-granulated
- $NiO/NiAl_2O_4$ 40/60, spray-dried
- $NiO/NiAl_2O_4/MgAl_2O_4$ 40/42/18, spray-dried
- $NiO/Mg\text{-}ZrO_2$ 40/60, freeze-granulated
- $Fe_2O_3/Mg\text{-}ZrO_2$ 60/40, freeze-granulated
- Colormax, up-concentration of Mn minerals
- Ilmenite, $FeTiO_3$ natural ore
- Iron oxide shells
- $CaMn_{0.88}Ti_{0.12}O_3$

Total time of operation: 776 h

Key results:

- **Successful operation with a number of materials**
- **Demonstration of syngas generation with partial oxidation with complete methane conversion (for chemical-looping autothermal reforming)**

Publications: 10

Korea Advanced Inst. of Science & Technology, ~1 kW

Dimensions:

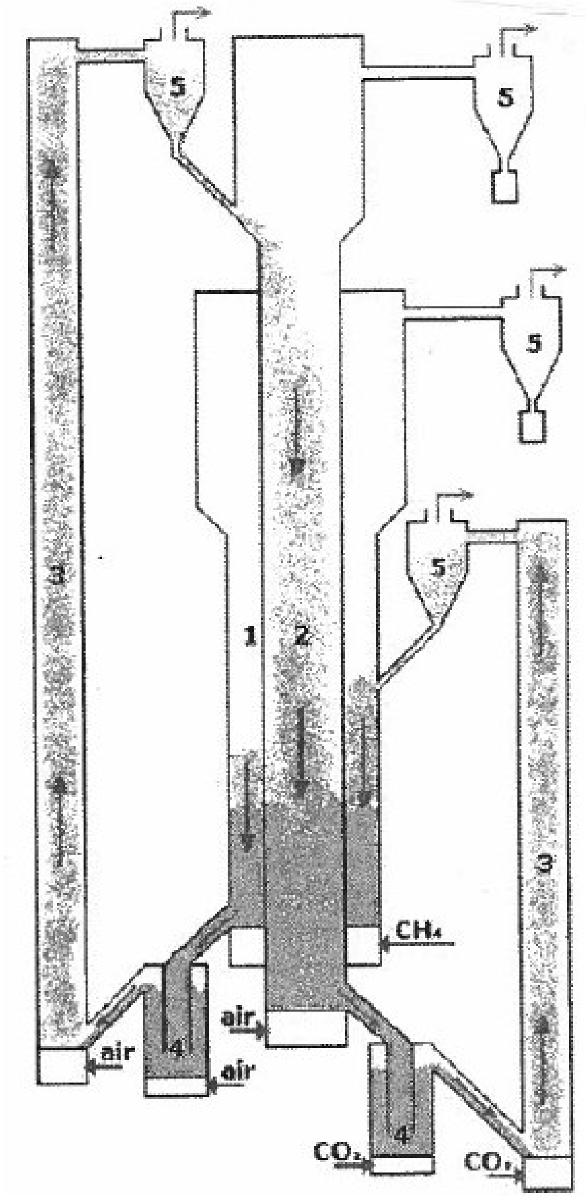
AR: Ø 23 mm, height 1.5 cm
FR: Ø 55 mm (with AR inside), height 0.9 m

Type:

Bubbling AR, bottom outflow via loop-seal
Bubbling FR, bottom outflow via loop-seal
AR inside FR (concentric tubes)
Risers circulating particles from AR and FR

Fuel: methane

First published: 2006



Oxygen carriers:

- $NiO-Fe_2O_3$/bentonite, NiO/Fe_2O_3 100/0
- $NiO-Fe_2O_3$/bentonite, NiO/Fe_2O_3 75/25
- $NiO-Fe_2O_3$/bentonite, NiO/Fe_2O_3 50/25
- $NiO-Fe_2O_3$/bentonite, NiO/Fe_2O_3 25/75
- $NiO-Fe_2O_3$/bentonite, NiO/Fe_2O_3 0/100

Total time of operation: ?

Key results:

- >95% conversion with NiO/Fe_2O_3 $\geq$50/50

Publications: 1

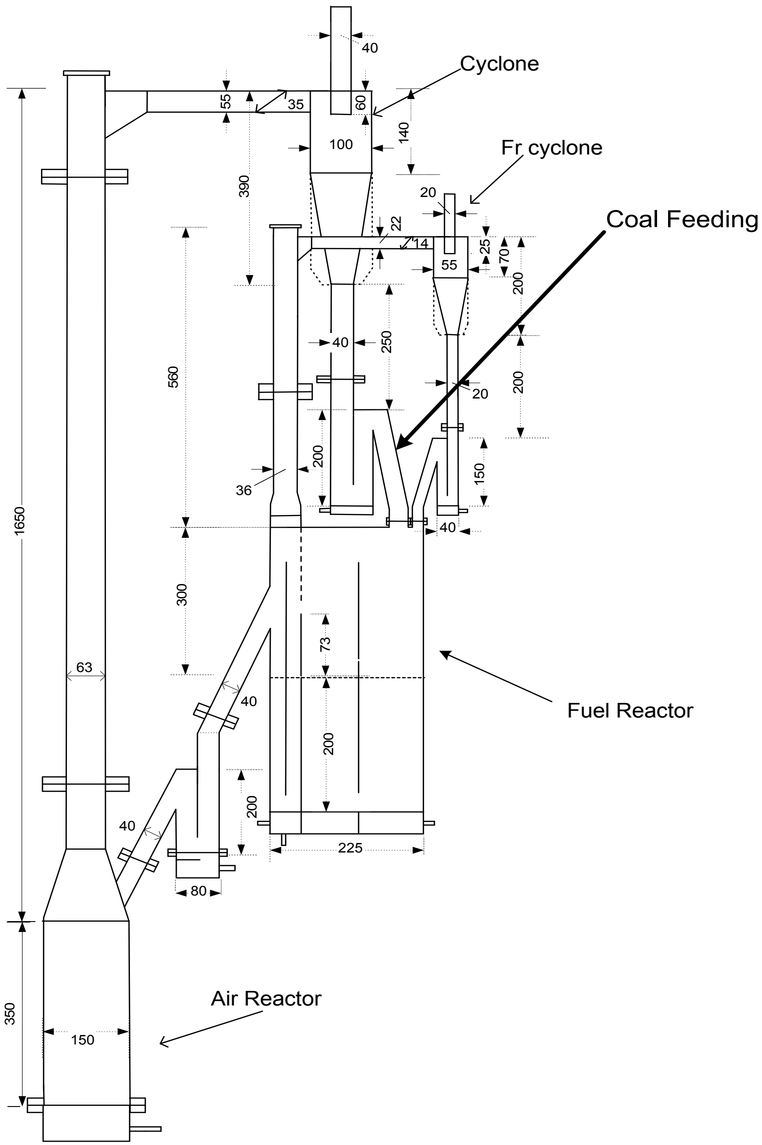
Chalmers 10 kW for solid fuels

Dimensions:
- AR: Ø 15 cm, riser 8 cm
- FR: 8x19 cm

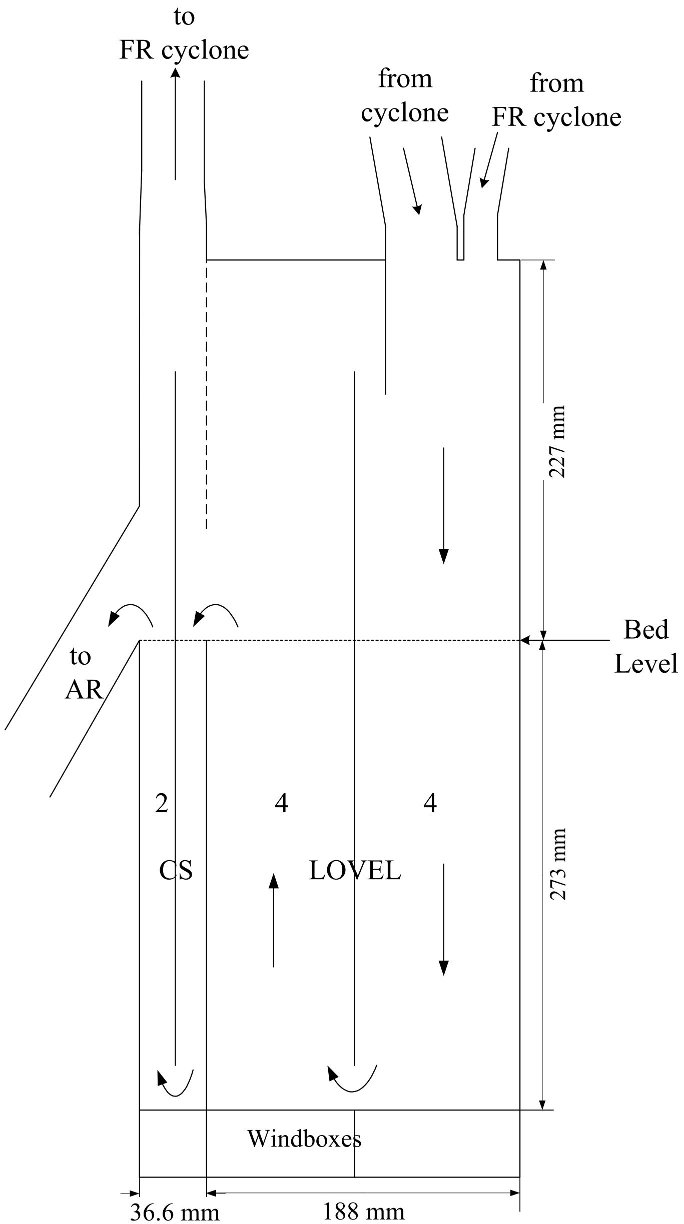
Type:
- Circulating AR
- Bubbling FR, with underwear to improve fuel residence time distribution
- Small carbon stripper, 36*44 mm, after FR
- Loop seals between AR and FR

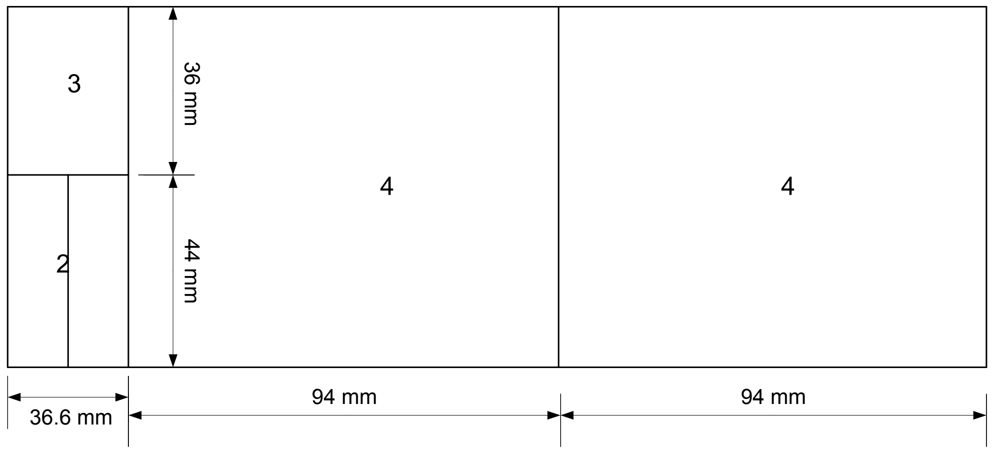
Fuel: petroleum coke, bituminous coal

First published: 2008



Fuel reactor, front and top view



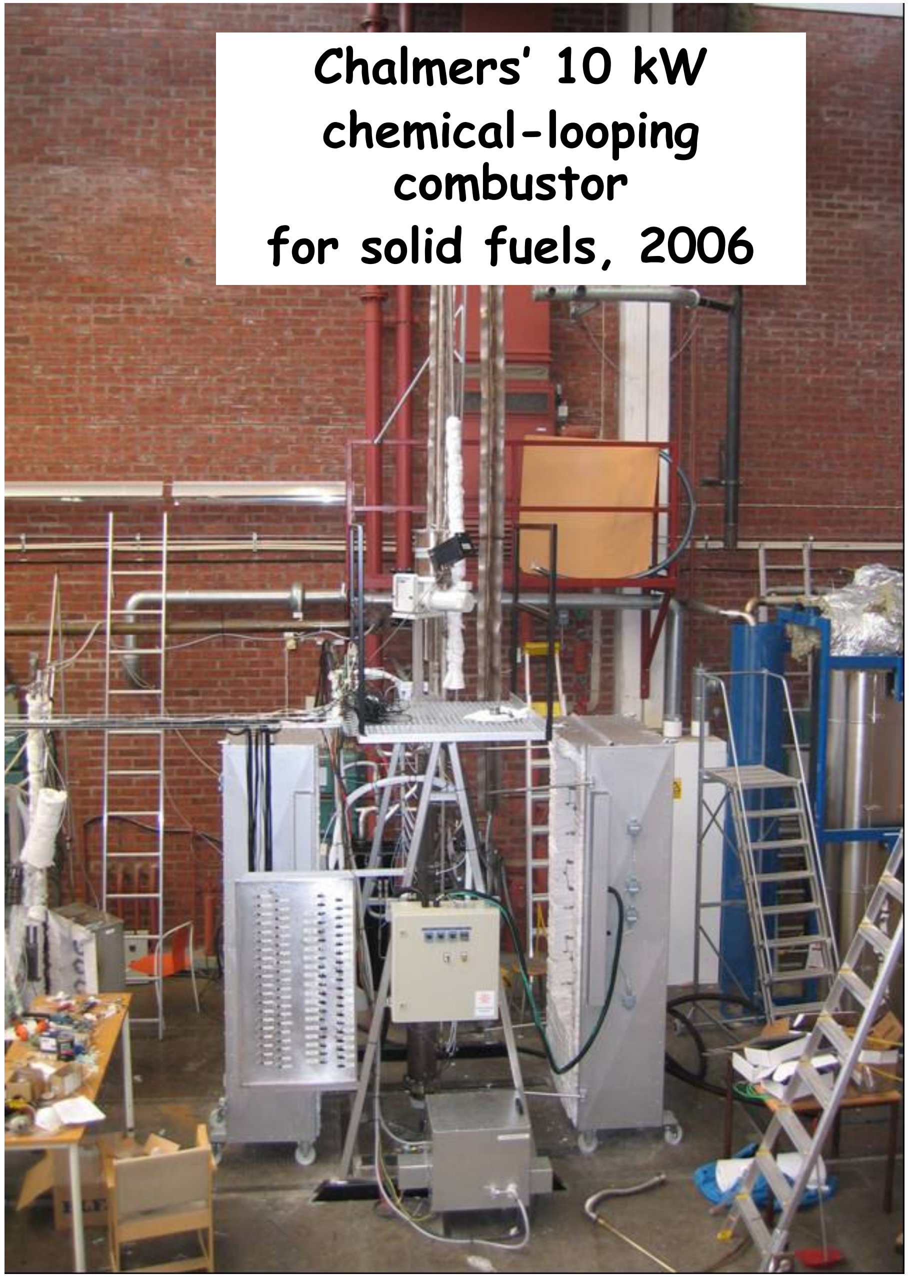


2 carbon stripper

3 high velocity part (below riser)

4 low velocity part, divided into two chambers, and fluidized by steam

Arrows indicate direction of particle circulation


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

Oxygen carriers:

Ilmenite

Total time of operation: 88 h

Key results:

- proof of concept, solid fuel *CLC*
- gas: incomplete oxidation (feeding causes volatiles release above bed)
- CO_2 from air reactor (from burning char)
- char loss (poor cyclone)
- cheap oxygen carrier, ilmenite, 100 €/ton

Publications: 6

CSIC-ICB Zaragoza, 500 W

Dimensions:

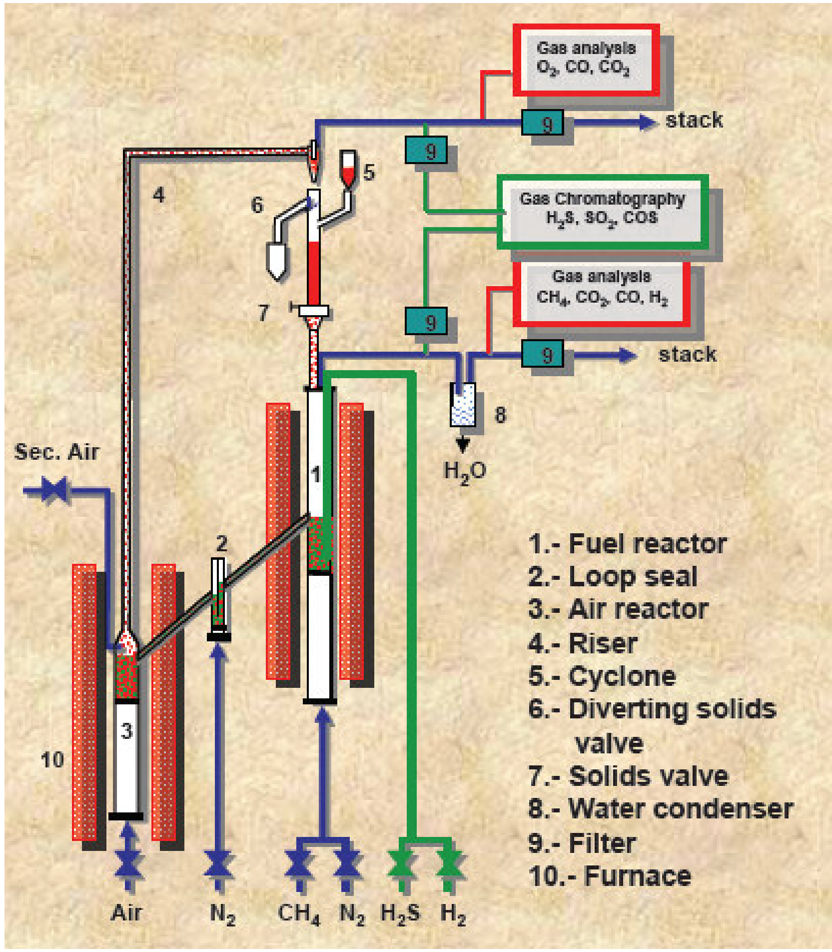
- AR: Ø 5 cm, riser 2 cm
- FR: Ø 5 cm

Type:

- Bubbling AR, particles entrained by narrow riser
- Bubbling FR, overflow exit
- Loop seal after FR
- Container + slide valve controls return flow to FR

Fuel: CH_4, CO, H_2, CO/H_2 (2:1 and 1:2), C_2H_6, C_3H_8, CH_4/C_2H_6 (4:1), CH_4/C_3H_8 (5:1), methane/H_2S (100, 300, 500, 800, 1000 ppm).

First published: 2008



Oxygen carriers:

NiO/γ-Al_2O_3 21/79, impregnation

NiO/α-Al_2O_3 18/82, impregnation

CuO/Al_2O_3 14/86, impregnation

Total time of operation: 660 h

Key results:

- **>98% CH_4 conversion for syngas production**
- **Effect of sulphur on NiO mapped**
- **No large difference between methane and other light hydrocarbons**

Publications: 8

Technical University of Vienna, 120 kW

Dimensions:

AR: Ø 15 cm, height 4.1 m

FR: Ø 16 cm, height 3 m

Type:

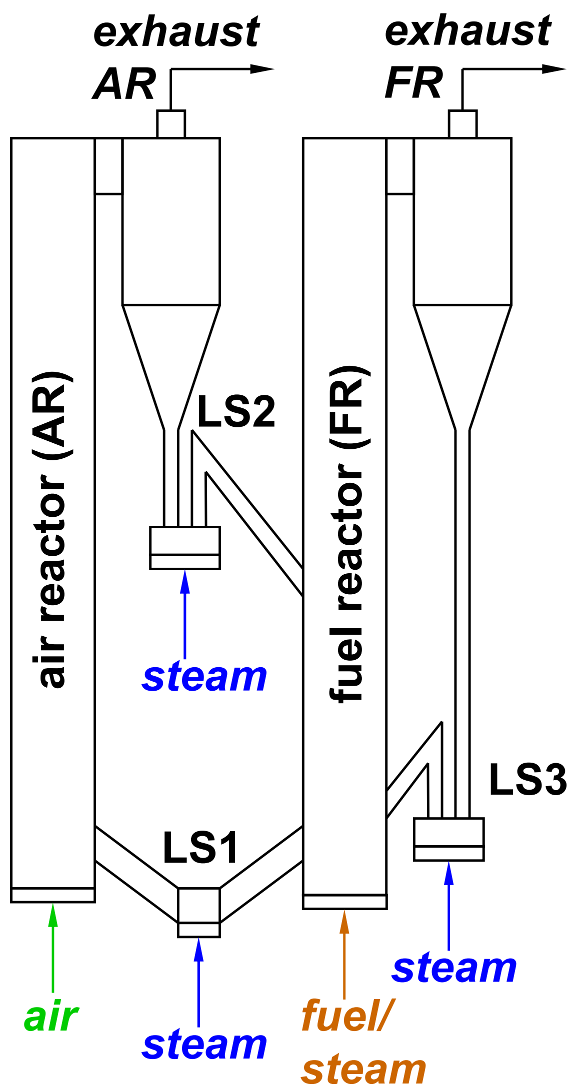
Circulating AR, outlet to FR

Circulating FR,

Outflow through FR bottom directly to AR through fluididized connection

Fuel: natural gas, CO, H_2

First published: 2009



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Oxygen carriers:

- Ilmenite
- $NiO/NiAl_2O_4$ 40/60, spray-dried
- $NiO/NiAl_2O_4/MgAl_2O_4$ 40/42/18, spray-dried

Total time of operation: 390 h

Key results:

- Operation at loads 20-145 kW,
- Operation at temperatures 780-960 C
- Operation at air ratios 0.8-1.25
- Fuel conversion: 95% (CH_4), 99% (H_2, CO)

Publications: 10

Alstom, 15 kW

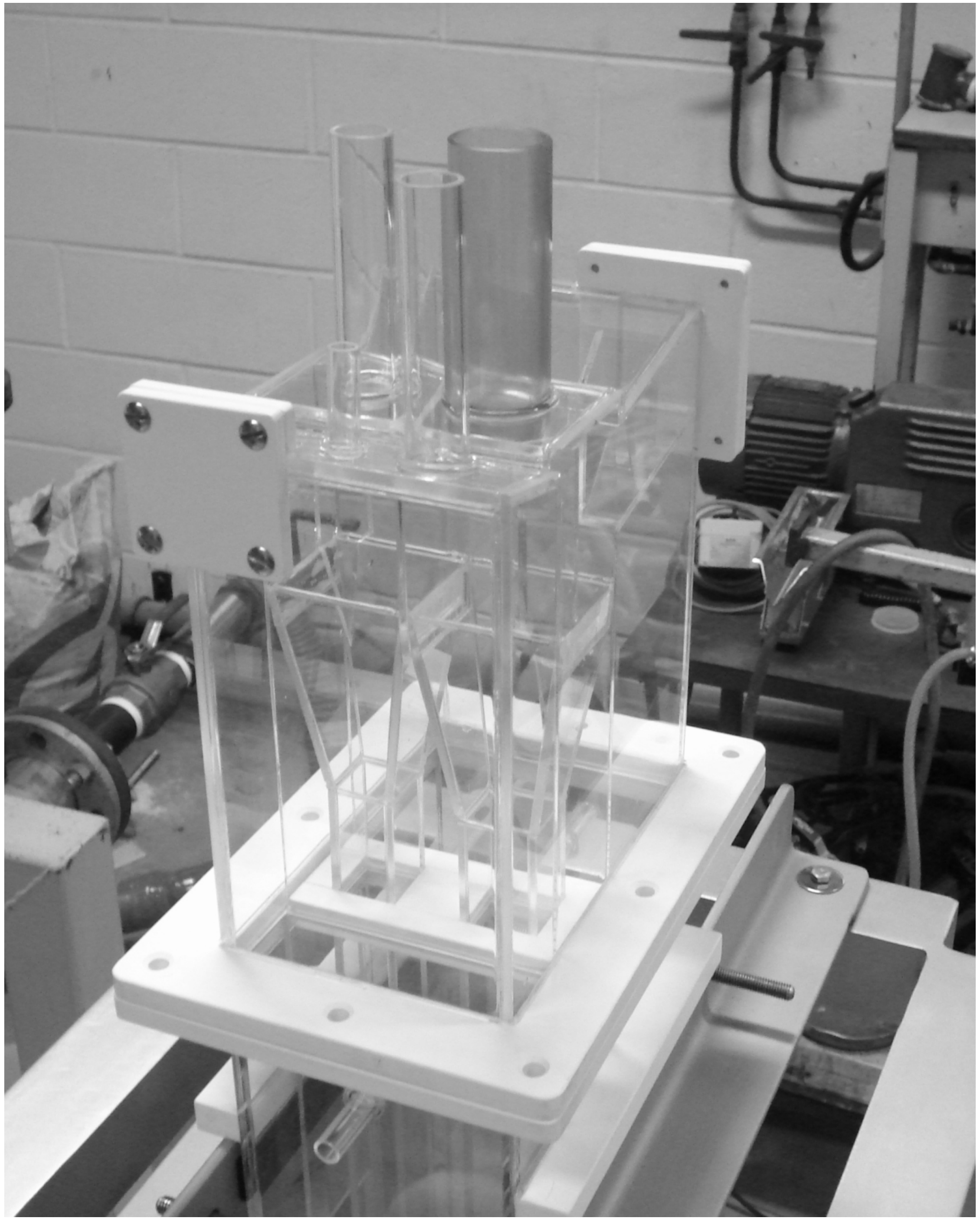
Dimensions:
not known

Type:
Circulating AR,
Circulating FR,
Highly integrated design.
Seal-pots with double outlets, one flow recycled, one to the other reactor.

Fuel: natural gas

First published: 2009

Alstom 15 kW cold flow model



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Oxygen carriers:

$NiO/NiAl_2O_4$ 40/60, freeze-granulated

$NiO/NiAl_2O_4$ 40/60, spray-dried

$NiO/NiAl_2O_4/MgAl_2O_4$ 40/42/18, spray-dried

NiO/Al_2O_3, impregnation

Total time of operation: 100 h

Key results:

methane conversion up to 99%

Publications: 1

Southeast University, Nanjing 10 kW solid fuel

Dimensions:

AR: Ø 5 cm, height 2 m

FR: 23x4 cm, height 1.5 m

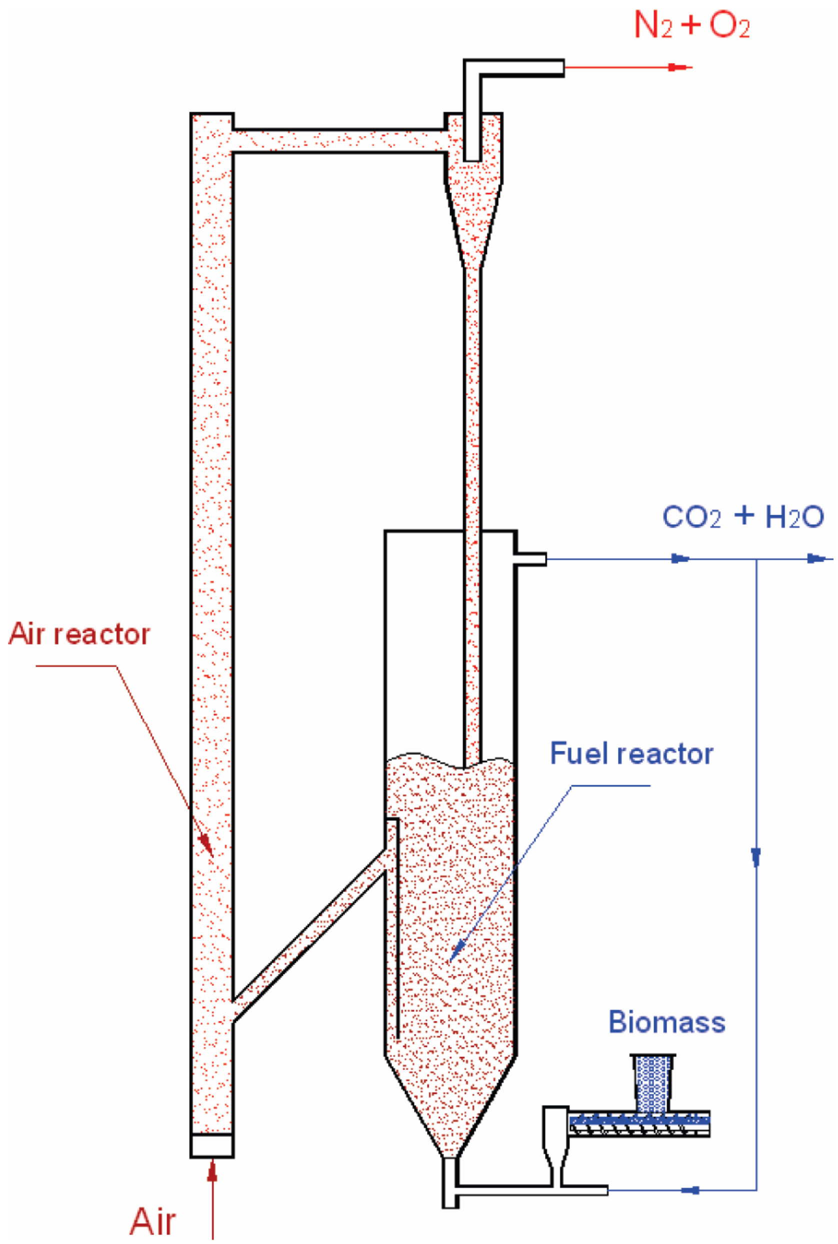
Type:

Circulating AR

Spouted FR, outflow via a special direct connection to AR

Fuel: Coal, biomass (pine sawdust),

First published: 2009



Oxygen carriers:

Fe_2O_3, sintered iron oxide powder

$NiO/NiAl_2O_4$ 33/67, impregnation

Total time of operation: 230 h

Key results:

Oxygen carrier deterioration (NiO) with coal but no effect with biomass

Publications: 4

Location	Unit	Oxides tested	Operation hours	Fuel	First publ.
Chalmers	10 kW	NiO, Fe_2O_3	1350	nat. gas	2004
KIER, S. Korea	50 kW	NiO, CoO	28	nat. gas	2004
CSIC, Spain	10 kW	CuO, NiO	140	nat. gas	2006
Chalmers	0.3 kW	NiO, Mn_3O_4, Fe_2O_3, ilmenite, $CaMnO_3$	730	nat. gas, syngas	2006
Daejong, S. Korea	1 kW	NiO + Fe_2O_3	a few	CH_4	2006
Chalmers	10 kW –SF	ilmenite	90	coal, petcoke	2008
CSIC, Spain	0.5 kW	CuO, NiO	660	nat. gas	2009
Vienna, Techn. Univ.	140 kW	ilmenite, NiO	390	nat. gas, CO, H_2	2009
Alstom	15 kW	NiO	100	nat. gas	2009
Nanjing	10 kW -SF	NiO, Fe_2O_3	>100	coal, biom.	2009

Conclusions

- >3700 h of operational experience
- 48 publications
- 10 different units, all worked
- 22 different materials (not all worked):
  - 14 Ni-materials
  - 7 Fe-materials
  - 3 Mn-materials
  - 1 Cu-material
  - 1 Co-material
  - 3 mixed Fe/Ni—materials
  - out of these were 3 ores/waste materials

Ni-materials

- high reactivity
- proven under long-term testing, >1000 h,
- large-scale manufacture and commercial raw materials verified
- thermodynamics restrict conversion to 99-99.5%

Cu-material

- High reactivity and complete methane conversion
- Tested > 100 h

Mn-materials

- good reactivity for methane, and high for CO/H_2
- $CaMn_{0.88}Ti_{0.12}O_3$ gives very good conversion and some CLOU effect (releases O_2)

Fe-materials

- poor reactivity towards methane, but good for CO/H_2
- generally more susceptible to agglomerations if reduced too far

Co-material

- high reactivity
- thermodynamically restricted to ~96%

Is CLC a break-through technology for CO_2 capture? (tick the appropriate box)

☐ **yes**

>100 publications on CLC to be found on:

http://www.entek.chalmers.se/~anly/co2/co2publ.htm

+ links to ICB-CSIC, TU-Vienna

More links to CLC publication lists are welcome!

Heartfelt gratitude to organizers

Thank you

Mercy beaucoup

Tack så mycket