PRESSURE BALANCE OF A MULTIPLE-LOOP CHEMICAL REACTOR

Trevor D. Hadley[*]   Ken Chiang[†]

Nick R. Burke[‡]   Kok-Seng Lim[**]

[*]CSIRO Process Science and Engineering, trevor.hadley@csiro.au

[†]CSIRO Process Science and Engineering

[‡]CSIRO Process Science and Engineering

[**]CSIRO Process Science and Engineering

PRESSURE BALANCE OF A MULTIPLE-LOOP CHEMICAL REACTOR

Trevor D. Hadley[1.], Ken Chiang[2.], Nick R. Burke[2.], Kok-Seng Lim[1.]
[1.] CSIRO Process Science and Engineering
[2.] CSIRO Petroleum
Bayview Avenue, Clayton, VIC 3168, Australia

ABSTRACT

For a chemical looping (CL) process it is important to determine the optimum reactor configuration that would offer good pressure balance to ensure smooth transfer of the solids between the reactor loops as well as satisfying the oxygen carrier and heat requirements. A variation of the CL process for production of enriched hydrogen stream is investigated which adopts multiple reactor loops. A pressure balance model is developed and a methodology is proposed to find a feasible reactor configuration at an industrial scale production of hydrogen.

INTRODUCTION

Chemical looping (CL) is reported as a promising technology for fossil fuel combustion because of its ability to produce a more concentrated carbon dioxide stream, enabling easier capture and sequestration. In such a system a metal oxide is used to oxidise the fuel instead of air. The reduced metal is then oxidised in a separate chamber and returned back to the combustion chamber. In this way the air and fuel do not make direct contact with each other and the resulting CO_2 and H_2O are kept separate from the N_2 and remaining O_2. The advantage of this arrangement is that the CO_2 is inherently separated from the N_2 thereby reducing the cost of separation prior to sequestration.

Researchers [1-3] have investigated CL combustion as an alternative means of preparing a CO_2 sequestration-ready stream. Of these, some have investigated the combustion of natural gas (CH_4) [4,5] while other have considered the combustion of syngas (CO and H_2) [6,7] and coal (with a NiO based oxygen carrier) [8]. Most of these have considered using two connected fluidized beds, however Noorman *et al* [5] have considered utilising two dynamically operated packed beds. CL can also be utilised for gasification and has been investigated, amongst others, as a means for gasifying coal [6,7] using Fe/FeO or CaO. Additionally, CL has been investigated as a means of producing hydrogen using steam [9,10].

A host of metals can be utilised as the oxygen carrier. However, transition metal oxides such as nickel, copper, cobal, iron and manganese are good candidates given their favourable reductive/oxidative thermodynamic properties. Hossain and de Lasa [11] presented a thorough review of CL combustion, including considerations of the choice of oxygen carrier, and compared these to current CO_2 capture techniques.

This paper investigates not only the mass and energy balance requirements of the CL process, but also the pressure balance in order to find a likely reactor geometry which will satisfy the many requirements including conversion and solids flux.

MODEL OF PRESSURE DROP

One of the key factors that affects the performance of the CL process is in achieving a good balance between solids recirculation rate required for the reaction as well as heat transfer. From the reactor design and operational consideration, it is important to determine the optimum reactor configuration that would offer good pressure balance to ensure smooth transfer of the solids between the reactor loops as well as satisfying the oxygen carrier and heat requirements. The pressure balance in turn is affected by variables such as the physical properties of the solid and gas, fluid velocity, solids recirculation rate and well as the geometry of the system.

Various methodologies have been reported to estimate the pressure drop through parts of a circulating fluidized bed (12,13). A one-dimensional model is used in this paper, as used by Lim *et al* (14). The chemical looping reactor (CLR) is divided into three main sections being the riser, downcomer and bubbling fluidized bed. The key pressure loss equations are summarised in Table 1.

Table 1. Key pressure loss equations (14).

Region	Factor	Equation	Ref
Riser	Static	$dP_{static} / dz = \rho_s (1 - \varepsilon) g$; $(\varepsilon - \varepsilon_d)/(\varepsilon^* - \varepsilon) = \exp((z - z_i)/Z_o)$	(15)
Riser base	Acceleration	$\Delta P_{accel} = G_s{}^2 / 2\rho_s$	(16)
Riser	Gas friction	$dP_{fg} / dz = 2 f_g \rho_g U_g{}^2 / D_t$	(12)
Riser	Solids friction	$dP_{fs} / dz = 2 f_s \rho_s (1 - \varepsilon) U_s{}^2 / D_t$	(12)
Riser	Exit bend	$\Delta P_{bend} = f_{bend} \rho_p (1 - \varepsilon) U_g{}^2$ where $f_{bend} = 0.375$	(17)
Cyclone		$\Delta P_{cyc} = \rho_g / 2.03 \left[U_1^2 \{1 + 2\phi^2 (2r_t / r_e - 1)\} + 2U_2^2 \right]$	(18)
Downcomer	Static	$\Delta P_{down} = \rho_s (1 - \varepsilon_{mf}) gh$, at U_{mf}	(19)
Solids valve		$\Delta P_{valve} = (G_s A_t)^2 / (C_{Do} A_o)^2 2\rho_s (1 - \varepsilon_{mf})$	(13)
Bubbling bed	Static	$\Delta P_{bubb} = \rho_s (1 - \varepsilon) gh$	(20)

HYDROGEN PRODUCTION VIA CHEMICAL LOOPING

Relatively pure hydrogen can be formed from a natural gas stream using chemical looping. The proposed arrangement is shown in Figure 1a. In this arrangement steam is reduced to form hydrogen in the Steam Reactor while natural gas is combusted in the Fuel Reactor to form CO_2 and water vapour. In terms of the circulating oxygen carrier, the Steam Reactor is often referred to as the oxidiser while the Fuel Reactor is referred to as the reducer. The heats of reaction are as follows:

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad \Delta H_{rxn}(700°C) = \text{-45 kJ/mol Fe}_3O_4 \quad (1)$$

$$CH_4 + 4Fe_3O_4 \rightarrow CO_2 + 2H_2O + 12FeO \qquad \Delta H_{rxn}(750°C) = \text{92 kJ/mol Fe}_3O_4 \quad (2)$$

For this investigation natural gas (essentially CH_4) has been chosen as the fuel while iron oxide has been chosen as a likely oxygen carrier. In the Steam Reactor hydrogen is formed from steam via the oxidation of FeO to Fe_3O_4. The Fe_3O_4 is reduced back to FeO in the Fuel Reactor in order to supply the oxygen required for the combustion of the natural gas. While the reaction in the Steam Reactor is exothermic, the reaction in the Fuel Reactor is endothermic and the heat requirement in the Fuel Reactor cannot be fulfilled by any heat from the Steam Reactor, except if the hot hydrogen stream were used to preheat the feed natural gas stream. Even if the natural gas were preheated to 250℃ there would be a heat deficit. Therefore a third loop has been proposed where a portion of the solids are heated to 900℃ via oxidation of the reduced metal with air and the combustion of fuel (if required). The solids return to the Fuel Reactor at an elevated temperature and therefore supply sensible heat to the Fuel Reactor as shown in Figure 1b.
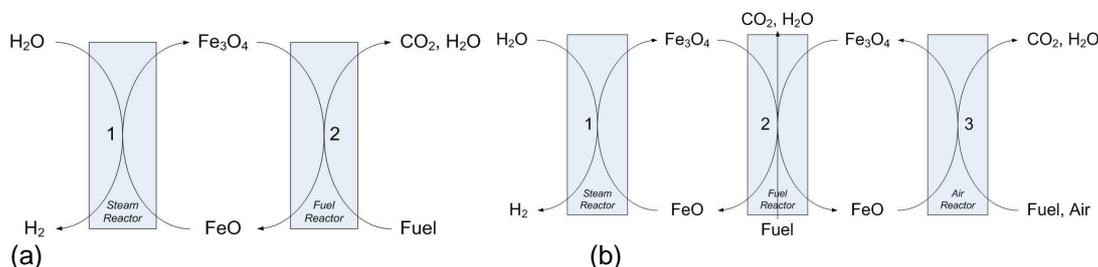

Figure 1. Schematic representation of the CL steam-iron process (a) two loops, (b) multiple loop

MASS AND ENERGY BALANCES

The main assumptions are contained in Table 2. Furthermore, the oxygen carrier was assumed to have a particle diameter of 160 μm. The associated minimum fluidization velocity (U_{mf}) was predicted using the approach of Wen and Yu [18] and determined as 19 mm/s temperatures between 700 and 1000℃. An oxygen carrier of the form $(Fe_2O_3)_x(CeO_2)_y(ZrO_2)_z$ has been chosen (x = 0.20, y = 0.13, z = 0.67).

Table 2. Some of the key assumptions for the proposed CL process.

	Steam Reactor	Fuel Reactor	Air Reactor
Reactor type	Riser	Bubbling Bed	Riser
Temperature	700℃	750℃	850 - 1000℃
Reaction	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$	$CH_4 + 4Fe_3O_4 \rightarrow CO_2 + 2H_2O + 12FeO$	$6FeO + O_2 \rightarrow 2Fe_3O_4$ $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$
Conversion	100% FeO to Fe_3O_4	100% Fe_3O_4 to FeO	100% FeO to Fe_3O_4
Excess		10% CH_4	8% O_2
Fuel preheat		CH_4 to 250℃	CH_4 to 250℃
Heat loss	10%	10%	10%

CASE STUDY

A methodology to evaluate the proposed CL steam-iron process and determine the likely reactor geometry is summarised in Figure 2. A hydrogen production rate of 49,000 Nm^3/h has been chosen based on an existing industrial scale reformer [21].

Mass and Energy Balance

The Steam Reactor generates slight excess heat. However adiabatic conditions can be achieved by cooling the returning solids stream from the Fuel Reactor from 750°C to 685°C. As predicted, the Fuel Reactor has a heat deficit which needs to be supplied via the sensible heat available in hotter solids from the Air Reactor. The additional oxidised metal fed to the Fuel Reactor (from the Air Reactor) also needs to be reduced using CH_4. The temperature of the returning solids (from the Air Reactor) strongly effects the overall CH_4 requirement, as shown in Figure 3 with less CH_4 required at higher temperatures.
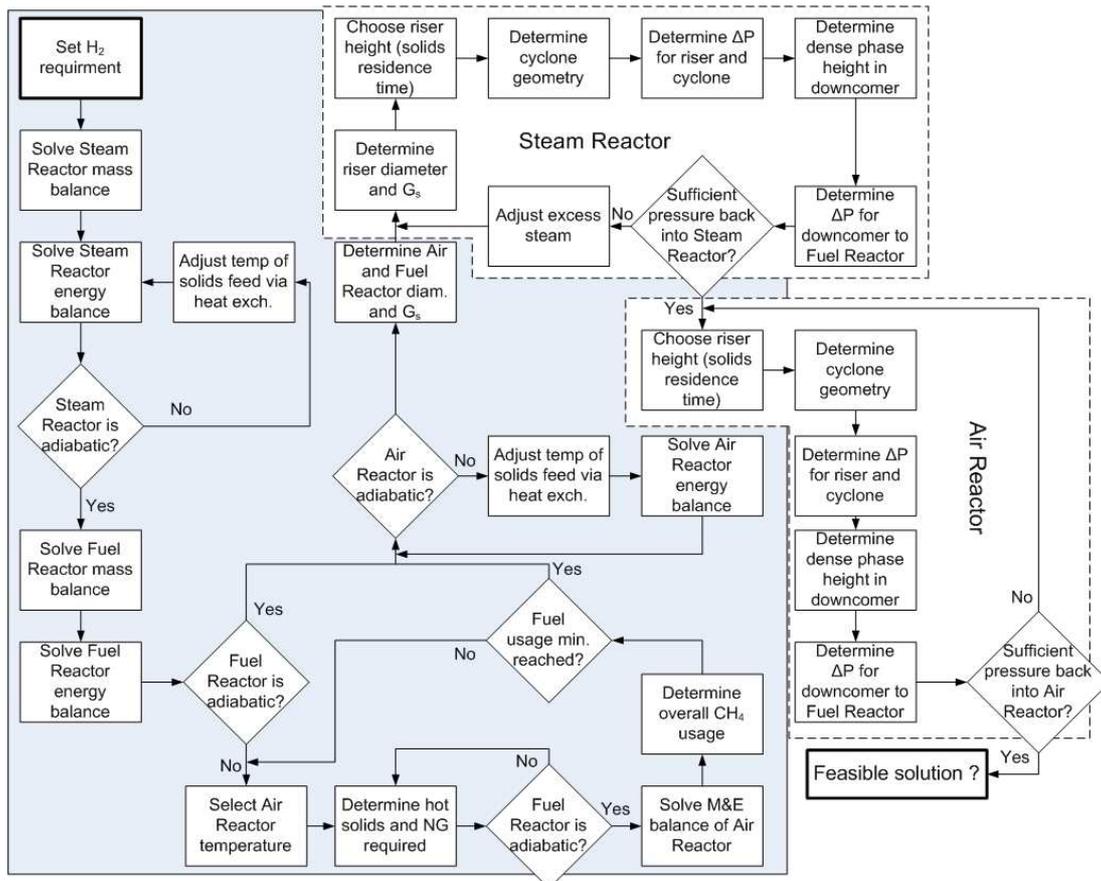

Figure 2. Proposed methodology for determining a multiple-loop chemical reactor configuration.

Below 1050°C the Air Reactor's heat can be supplied entirely via the air oxidation of FeO. However, above this temperature additional heat is required via the combustion of CH_4. While this does increase the overall CH_4 requirement, its effect is minimal in the 1050 – 1200°C range. However, com busting CH_4 in the Air Reactor is undesirable as it produces CO_2 which will be in a dilute form together with the nitrogen and unreacted oxygen. The optimum temperature for this particular arrangement is 1050°C, however a slightly more cons ervative temperature of 1000°C was adopted in this study and hence the Air Reactor has a slight excess of heat. This is balanced by cooling the entering solids stream from the Fuel Reactor to 705°C (from 750°C) before it enters the Air Reactor .
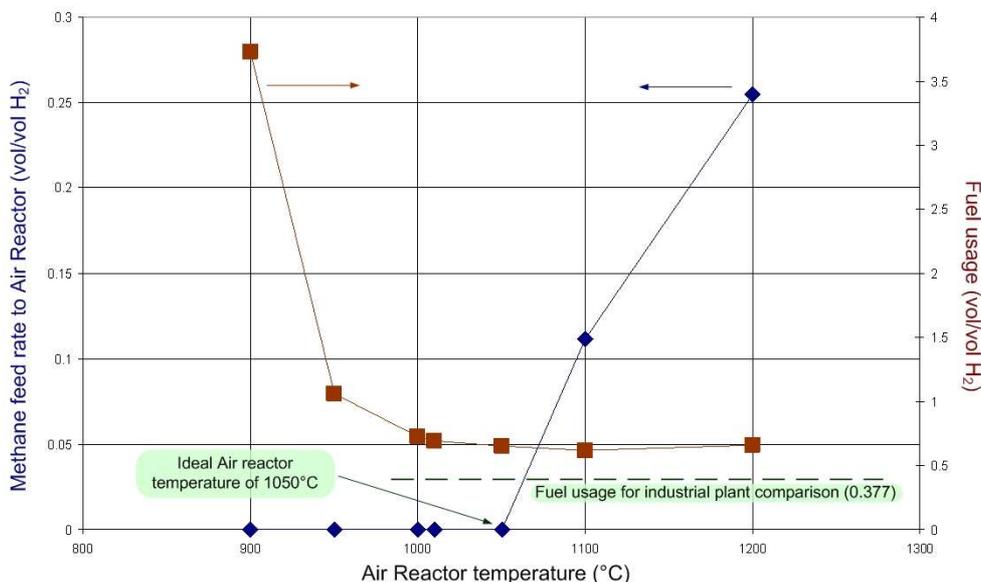
Figure 3. Fuel usage as a function of the temperature in the Air Reactor.

In comparison to a typical industrial hydrogen reformer, the current CL process configuration requires more fuel with a minimum of 0.62 Nm^3 of CH$_4$ required per Nm^3 of H$_2$ produced (compared to 0.38 (22)). Because CL is considered an alternative to other methods of concentrating the CO$_2$ stream and making it sequestration-ready, this additional cost should be compared to the cost incurred in processes such as ammonia scrubbing.

Pressure Balance
Based on the cyclone geometry, the riser and bed diameters, initial estimates of the riser and bed heights as well as the relative heights and positions of the reactors, downcomers and loop seals, an initial pressure balance can be determined across the entire system using the assumptions in Table 1.

The high solids flux through the Steam Reactor resulted in a high pressure drop across the riser. The taller the riser is, the more difficult it becomes to design the system such that the pressure at the bottom of the Fuel Reactor is still sufficiently above the pressure at the entrance to the steam riser. The height was set in order to achieve a solids residence time of more than a minute. The resulting riser pressure drop was too high and was solved by increasing the amount of excess steam used for the oxidation of the FeO. This excess steam would need to be condensed from the hydrogen produced and then recycled back to the Steam Reactor. The resultant mass balance is given in Figure 4.

Finally, in order to complete the pressure balance, the freeboard of the Fuel Reactor needs to be operated at 1.1 bar (gauge) and the downcomers need to be operated with more than 50% of the height occupied by the dense phase. The pressure balance is shown in Figure 5. However, the current pressure balance gives no consideration to the solids refluxing effect at the exit of the riser, or to the pressure change at the entry to the riser from the loop seal.

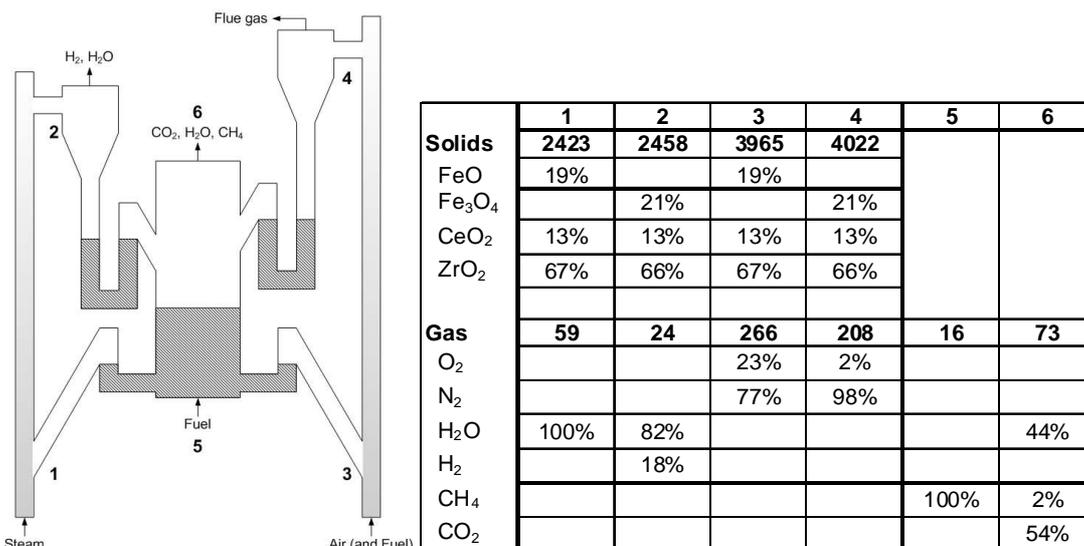|	**1**	**2**	**3**	**4**	**5**	**6**
Solids	2423	2458	3965	4022		
FeO	19%		19%			
Fe_3O_4		21%		21%		
CeO_2	13%	13%	13%	13%		
ZrO_2	67%	66%	67%	66%		
Gas	59	24	266	208	16	73
O_2			23%	2%		
N_2			77%	98%		
H_2O	100%	82%				44%
H_2		18%				
CH_4					100%	2%
CO_2						54%

Figure 4. Possible schematic of CL arrangement, and mass balance used for hydrogen production. Flows are in tons per hour and compositions in mass percentage.
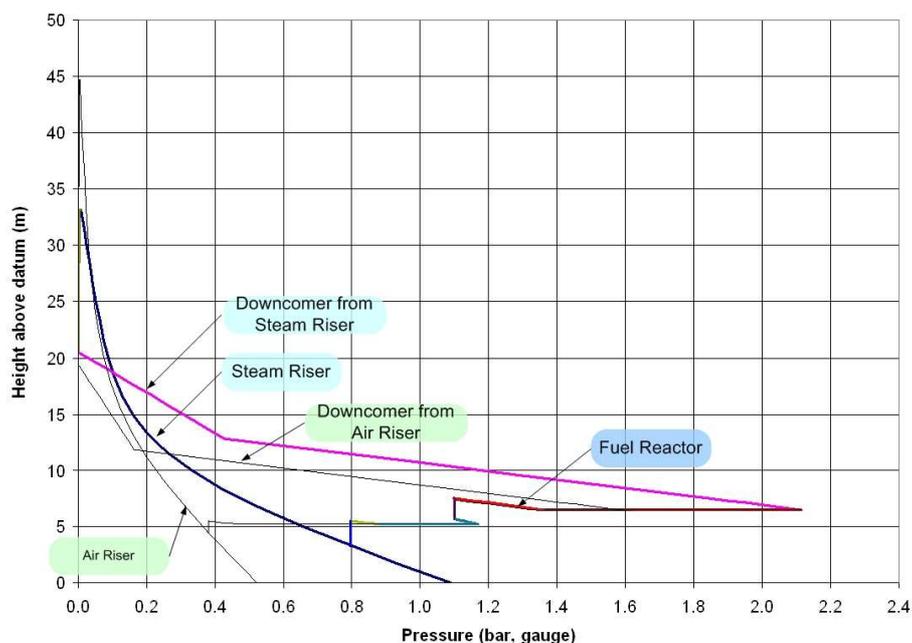

Figure 5. Pressure balance obtained over the CL system.

The gas flow rates influence the cyclone dimensions leading to heights of 12.6 and 25.3 m (based on standard cyclone design techniques) for the steam and Air Reactors respectively and hence determining the minimum heights for the two risers and downcomers. The final design is presented in Table 3.

CONCLUSIONS

A reactor design methodology has been proposed for a multiple-loop chemical reactor. The methodology takes into account the mass and energy and the pressure balance of the overall system. This approach has then been applied to examine a

possible reactor configuration for the production of hydrogen from natural gas while simultaneously producing a concentrated CO_2 stream that can be sequestration-ready. The methodology has shown that a feasible design can be obtained for the steam-iron process. However, there are cost penalties involved – cooling of the solids streams to the Steam and Air Reactors; increased methane usage for an equivalent hydrogen production when compared with an established hydrogen reformer; and an increased steam usage which necessitates recondensing and recycling. For true cost benefit analysis, these additional costs should be compared to the additional costs incurred in alternative CO_2 concentration and capture techniques.

Table 3. Likely reactor configuration for CL steam-iron hydrogen production.

		Steam Riser	Down-comer	Fuel Reactor	Air Riser	Down-comer	Units
Gas flow	entering	73496	173	35526	206202	553	Nm^3/h
	exiting	35681	101	96891	109900	308	Nm^3/h
Superficial gas velocity		6.0	0.1	0.4	6.0	0.1	m/s
G_s	entering	115		39	38		$kg/m^2.s$
	exiting	117		39	38		$kg/m^2.s$
Internal diameter		2.7	1.2	7.6	6.1	2.4	m
Temperature		700	700	750	1000	750	°C
Pressure	bottom	109	211	117	52	162	kPa,g
	top	0.85	0.05	110	0.37	0.05	kPa,g
Height							
Total internal		40			60		m
Gas exit		6.8			15.3		m
Downcomer (not including cyclone)			14			13	m
Bubbling bed /loop seal			1.0	0.5		1.0	m
Height relative to datum							
Bottom		0.0	6.5	5.2	0.0	4.4	m
Loop seal entrance to risers		3.3			4.5		m
Solids voidage (ε)		0.94	0.47	0.72	0.98	0.47	

NOTATION

A	cross-sectional area	m^2		r_e	radius of exit pipe	m
C_D	discharge coefficient	-		r_t	radius of circle to which centre line	
D_t	riser diameter	m			is tangential	m
f	friction factor	-		U	superficial velocity	m/s
g	gravitational constant	m/s^2		z	height in riser	m
G_s	solids flux	$kg/m^2.s$		z_i	location of point of inflection	m
h	bed height	m		Z_o	characteristic length	m
P	pressure	Pa				

Greek

ρ_s	particle density	kg/m^3		$\o$	factor used in calculation	-
ε	voidage fraction	-				

Subscripts

*	asymptotic lean phase		g	gas	
1	inlet duct		mf	minimum fluidization	
2	exit duct		t	vessel emptying out to	
d	dense phase		o	opening/orifice	
f	friction				

REFERENCES

1. P. Cho, T. Mattisson, A. Lyngfelt, Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion, *Fuel,* **83** 9 (2004) 1215-1225.
2. F. He, H. Wang, Y. Dai, Application of Fe2O3/Al2O3 Composite Particles as Oxygen Carrier of Chemical Looping Combustion, *Journal of Natural Gas Chemistry,* **16** (2007) 155-161.
3. A. Lyngfelt, B. Leckner, T. Mattisson, A fluidized-bed combustion process with inherent CO2 separation; application of chemical-looping combustion, *Chemical Engineering Science,* **56** 10 (2001) 3101-3113.
4. A. Abad, T. Mattisson, A. Lyngfelt, M. Johansson, The use of iron oxide as oxygen carrier in a chemical-looping reactor, *Fuel,* **86** 7-8 (2007) 1021-1035.
5. S. Noorman, M. van Sint Annaland, H. Kuipers, Packed Bed Reactor Technology for Chemical-Looping Combustion, *Industrial & Engineering Chemistry Research,* **46** 12 (2007) 4212-4220.
6. L. Fan, F. Li, S. Ramkumar, Utilization of chemical looping strategy in coal gasification processes, *Particuology,* **6** 3 (2008) 131-142.
7. F.X. Li, L.S. Fan, Clean Coal Conversion Processes - Progress and Challenges, *Energy & Environmental Science,* **1** 2 (2008) 248-267.
8. L. Shen, J. Wu, J. Xiao, Experiments on chemical looping combustion of coal with a NiO based oxygen carrier, *Combustion and Flame,* **156** 3 (2009) 721-728.
9. M.F. Bleeker, S.R.A. Kersten, H.J. Veringa, Pure hydrogen from pyrolysis oil using the steam-iron process, *Catalysis Today,* **127** 1-4 (2007) 278-290.
10. E. Lorente, J.A. Peña, J. Herguido, Kinetic study of the redox process for separating and storing hydrogen: Oxidation stage and ageing of solid, *International Journal of Hydrogen Energy,* **33** 2 (2008) 615-626.
11. M. Hossain, H.I. de Lasa, Chemical-looping combustion (CLC) for inherent CO2 separations - a review, *Chemical Engineering Science,* **63** 18 (2008) 4433-4451.
12. R.W. Breault, V.K. Mathur, High-Velocity Fluidized-Bed Hydrodynamic Modeling .2. Circulating Bed Pressure-Drop Modeling, *Industrial & Engineering Chemistry Research,* **28** 6 (1989) 688-693.
13. M. Horio, Hydrodynamics, In: Circulating Fluidized Beds, (Ed. J.R. Grace, A.A. Avidan and T.M. Knowlton), Springer, New York, (1996).
14. K.S. Lim, P. Peeler, R. Close, T. Joyce, Estimation of Solids Circulation Rate in CFB From Pressure Loop Profiles, *6th International Conference on Circulating Fluidized Beds.* Frankfurt, Germany (1999) 819-824.
15. Y. Li, M. Kwauk, The Dynamics of Fast Fluidization, In: Fluidization, (Ed. J.R. Grace and J.M. Matsen), Plenum Press, New York, (1980).
16. H.T. Bi, J.X. Zhu, Static Instability Analysis of Circulating Fluidized-Beds and Concept of High-Density Risers, *AICHE Journal,* **39** 8 (1993) 1272-1280.
17. C.E. Capes, K. Nakamura, Vertical Pneumatic Conveying - Experimental Study With Particles in Intermediate and Turbulent-Flow Regimes, *Canadian Journal of Chemical Engineering,* **51** 1 (1973) 31-38.
18. D. Kunii, O. Levenspiel, Fluidization Engineering, Butterworth-Heinemann, Boston, (1991).
19. R.K. Sinnott, Chemical Engineering Design, 4th ed. , Elsevier Butterworth-Heinemann, New York, (2005).
20. D.R.M. Jones, J.F. Davidson, The flow of particles from a fluidised bed through an orifice, *Rheologica Acta,* **4** 3 (1965) 180-192.
21. C.Y. Wen, Y.H. Yu, A Generalized Method for Predicting Minimum Fluidization Velocity, *AICHE Journal,* **12** 3 (1966) 610-612.
22. H. Olsson, P. Rudbeck, K.H. Andersen, Adding Hydrogen Production Capacity by Heat Exchange Reforming, *XIV Refinery Technology Meet (RTM).* Kovalam, Trivandrum, India (2007).