Engineering Conferences International
ECI Digital Archives

10th International Conference on Circulating Fluidized Beds and Fluidization Technology - CFB-10

Refereed Proceedings

Spring 5-2-2011

Design Requirements for Pressurized Chemical Looping Reforming

Tobias Pröll
Vienna University of Technology, tobias.proell@tuwien.ac.at

Hermann Hofbauer
Vienna University of Technology, Austria

K. Marx
Vienna University of Technology, Institute of Chemical Engineering

DESIGN REQUIREMENTS FOR PRESSURIZED CHEMICAL LOOPING REFORMING

K. Marx, T. Pröll and H. Hofbauer
Vienna University of Technology, Institute of Chemical Engineering,
A-1060 Vienna, Austria

ABSTRACT

A key issue in chemical looping reforming is to operate the process under pressurized conditions. Applicability of dual fluidized bed systems, currently used in atmospheric chemical looping processes, is affected by pressure. Critical design issues were studied and experimentally verified by cold flow model experiments. It turns out that it is important to achieve sufficient global solids circulation and to keep the pressure difference between the reactors low enough for proper operation of the loop seals.

INTRODUCTION

Hydrogen is an important raw material for production of basic chemicals, in oil refining, and many other industrial applications. Although naturally occurring, most of the hydrogen used is produced from fossil raw materials (1). Catalytic steam reforming of hydrocarbons is currently the cheapest way to produce hydrogen and accounts for more than 90% of the world's hydrogen production. In such systems heat transfer is a key issue to improve the process performance (2).

Chemical looping combustion (CLC) recently attracted interest as a carbon capture technology. A variant of the process is chemical looping reforming (CLR) where less oxygen than required for complete combustion is supplied. In chemical looping two separate reaction zones, an air reactor (AR) and a fuel reactor (FR) are available. A metallic solid is kept in circulation between the reactors, usually called oxygen carrier (OC). The solids are used to transport oxygen and heat and, especially in CLR, also act as a reforming catalyst. While in CLC full conversion of the fuel is intended, a syngas is produced in CLR.

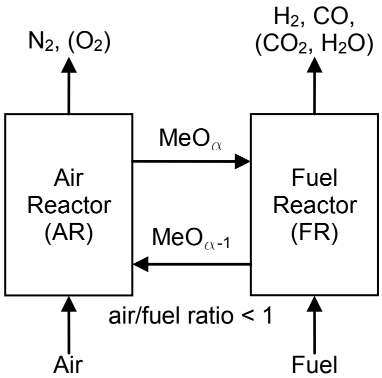

Fig. 1 Chemical looping reforming principle

The CLC process has been intensively studied over the recent years (3-4). Many different oxygen carrier materials have been tested (3-5) and the technology has been demonstrated for more than 1000h (6) and at scales of up to 150kW (7). Dual fluidized bed (DFB) systems have been applied to the process claiming to fit the requirements of chemical looping the best (8-9).
Nickel based oxygen carriers are beneficial in CLR because of their high catalytic activity towards methane steam reforming. Promising results have been obtained with such oxygen carriers at atmospheric conditions (10-11). Thermodynamic

equilibrium has been reached and no coke formation has been observed even at very low steam to carbon ratios in the FR feed. Pröll et.al. (11) addressed the main advantages of CLR compared to catalytic steam reforming to be:

- Heat required in the reactions is supplied inherently, no external heating is needed, thus no heat transfer limitations are expected.
- Less steam is required.
- Fewer concerns with respect to sulfur contaminants (12).

A key issue in CLR is to operate the process at pressurized conditions (PCLR). Dual fluidized bed systems have never been applied to pressurized systems. Considerable operational limitations occurring from reactor pressure difference and solids throughput are expected. In this study limitations occurring from pressure were addressed and critical design issues in PCLR were identified. Cold flow model tests at conditions corresponding to pressurized conditions were carried out in an atmospheric dual circulating fluidized bed system.

CHEMICAL REACTIONS

The main reaction occurring in the air reactor is the oxidation of the oxygen carrier which is in case of a nickel based oxygen carrier:

$$Ni + \frac{1}{2}O_2 \rightleftharpoons NiO \qquad \Delta H_R^{900°C} = -234.6\,kJ/mol \qquad \text{(reac. 1)}$$

The situation inside the fuel reactor is governed by many reactions taking place in parallel or consecutively. The most relevant catalytic activated gas-phase reactions are the steam reforming and CO-shift reactions. Which, for methane will be:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_R^{900°C} = 225.6\,kJ/mol \qquad \text{(reac. 2)}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_R^{900°C} = -33.1\,kJ/mol \qquad \text{(reac. 3)}$$

The heat needed is supplied either by oxidation of reforming products or fuel with the metal oxide, or by the circulating solids transporting heat from the AR to the FR.

$$CH_4 + NiO \rightleftharpoons CO + 2H_2 + Ni \qquad \Delta H_R^{900°C} = 211.6\,kJ/mol \qquad \text{(reac. 4)}$$

$$CO + NiO \rightleftharpoons CO_2 + Ni \qquad \Delta H_R^{900°C} = -47.2\,kJ/mol \qquad \text{(reac. 5)}$$

$$H_2 + NiO \rightleftharpoons H_2O + Ni \qquad \Delta H_R^{900°C} = -14.0\,kJ/mol \qquad \text{(reac. 6)}$$

Practically, in CLR just enough air will be supplied to the AR to keep the desired operating temperature. The oxygen transport can be varied without influencing the global heat balance if a fraction of the fuel is fed to the AR. In this way the oxygen transport can be theoretically reduced to zero. From the principle of Le Chatelier it is evident that in equilibrium the methane content decreases with increasing temperature and higher steam ratios, and the methane content increases with pressure. Thus to improve the methane conversion high temperatures, high excess steam and low pressure are favorable. Compared to conventional catalytic methane steam reforming methane breakthrough at increased pressure can be avoided by increasing the FR temperature in PCLR.

CHALLENGES AT INCREASED PRESSURE

With increasing pressure, the gas density increases while the solids properties remain unchanged. This means that, for a certain gas mass flow rate, either the riser cross section or the superficial gas velocity will decrease with increasing pressure, both resulting in lower solids entrainment rates. The main challenges with respect to pressurized chemical looping reforming therefore are:

- The higher gas-solids reaction intensity.
- The fluidizing velocities must be kept within reasonable limits.
- The increased solids flux.
- Proper sealing between the reactors by the loop seals.

AR off-gas recycling is necessary to limit the solids throughput per cross section area in the AR as depicted in Fig. 2. The power demand of the recycle blower is expected to be low because of the low compression pressure ratio. Anyhow, the recycle gas stream has to be kept low to reduce the energy penalty from gas re-heating. This requires optimization of the ratio of solids circulation rate relative to gas velocity in the AR riser. The loop seals have to be designed considering dynamic backpressure changes from the two exhaust lines. Therefore, deep loop seals which can handle significant level changes are required. In addition an active control setup of the backpressure is necessary for proper operation of the system.

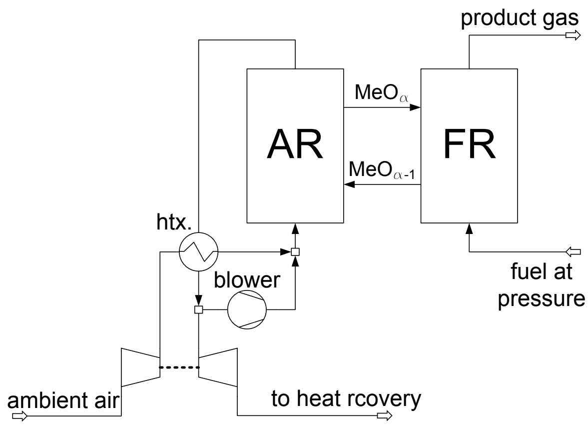

Fig. 2 Proposed PCLR arrangement.

EXPERIMENTAL

An existing dual circulating fluidized bed cold flow model (CFM) erected to study the dual circulating fluidized bed (DCFB) concept for chemical looping at atmospheric conditions (13) was modified and operated at conditions simulating pressurized conditions. A schematic drawing of the cold flow model is shown in Fig. 3. The system includes two risers, the air reactor and the fuel reactor, and three loop seals, the upper-, lower-, and internal loop seal. The CFM is a model of the existing hot 120 kW chemical looping pilot unit at Vienna University of Technology at a scale of 1:3. It is built of transparent acrylic glass allowing visual observation of the fluid dynamic pattern. 23 pressure probes were placed and connected to a personal-computer assisted measurement equipment. Solids circulation rates are measured by stopping the loop seal fluidization and measuring the rate of solids accumulation inside the appropriate downcomer. More specific details about the cold flow model can be found elsewhere (13).

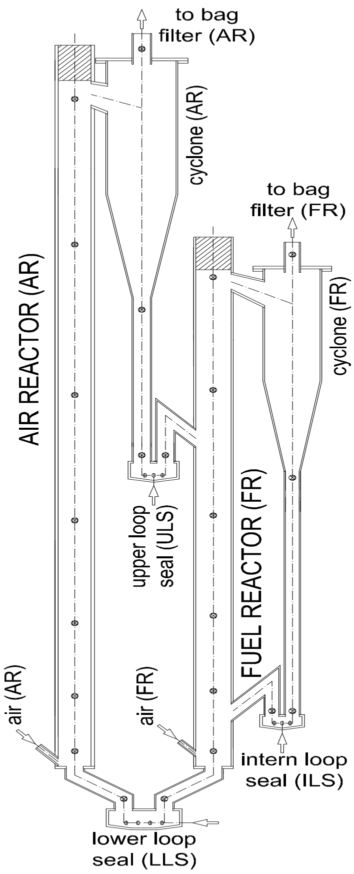

Fig. 3 Sketch of the DCFB CFM with pressure measurement ports indicated by dots.

Table 1 Characteristic design parameters of the system

	Hot unit		CFM		Unit
	AR_H	FR_H	AR_C	FR_C	
Type of gas	air	syngas	air	air	-
Reactor inner diameter	50	51	50	54	mm
Superficial gas velocity	6	3	5.75	9	m/s
Operation pressure	10	10	1.013	1.013	bar(a)
Operation temperature	1000	900	25	25	°C
Particle definition	Ni/NiO 40wt% NiO 60wt% $NiAl_2O_4$		Polystyrene		-
Particle mean diameter	120		110		µm
Particle density	3250		1050		kg/m³
Spericity	0.99		0.99		-

The Glicksman criteria (14) are a set of dimensionless numbers which are used to maintain hydrodynamic similarity in the cold flow model and the corresponding hot unit. The necessity of gas-solids density ratio similarity requires very light weight particles to simulate pressurized conditions in the atmospheric CFM fluidized with air. For good agreement with the Glicksman criterion polystyrene particles were used with a density of 1050 kg/m³ and a Sauter mean diameter of 110 µm. To avoid buildup of electrostatic forces ATMER 163, an anti-static agent, was added. The dimensions of the hot unit are subjected to detailed mass and energy balance investigations of a 150 kW methane input pilot PCLR unit operated at 10 bar(a) pressure where equilibrium of the reactions is reached theoretically. The dimensions and important parameters of the hot unit as well as the corresponding cold flow model are summarized in Table 1. For the given CFM geometry only the air reactor agrees well with similarity rules, shown in Table 2. Considering that the FR flow regime has a minor effect on the global system loop (13) the cold flow model can be used for investigating the behavior of the global solids loop with little error.

Table 2 Comparison of dimensionless groups

Parameter	Definition	Hot unit		Cold unit		Hot/Cold	
		AR_H	FR_H	AR_C	FR_C	AR	FR
Re_p	$\frac{d_p \cdot U_0 \cdot \rho_g \cdot \psi}{\eta_g}$	39.3	15.5	40.4	63.2	0.97	0.24
Ar	$\frac{\rho_g \cdot (\rho_p - \rho_g) \cdot {d_p}^3 \cdot g}{{\eta_g}^2}$	65.3	7.6	48.1	48.1	1.35	0.16
Fr	$\frac{{U_0}^2}{g \cdot d_p}$	$3.0 \cdot 10^4$	$7.5 \cdot 10^4$	$3.0 \cdot 10^4$	$7.5 \cdot 10^4$	1	1
density ratio	$\frac{\rho_p}{\rho_g}$	1265.8	2355.3	903.9	903.8	1.4	2.6
diameter ratio	$\frac{D}{d_p}$	416.7	425	454.5	490.9	0.92	0.87
spericity	ψ	0.99	0.99	0.99	0.99	1	1

RESULTS AND DISCUSSION

Observed pressure profiles

The pressure profile of fluidized beds can be used to identify design problems and to determine the solids distribution within the system. A typical pressure profile of the

CFM in operation is shown in Fig. 4. The low density of the particles used caused that the observed overall pressures are relatively low in the range of 15 mbar. The solids distribution curve of a typical circulating fluidized bed has a lower dense region and a lean upper section. Derived from momentum balance it is evident that in steady-state conditions the decay of the pressure profile indicates the solids inside the volume. Thus, typically a pressure profile in a CFB unit has a shape of high pressure gradients at the lower and low gradients at the upper section. On the other hand in dilute phase or pneumatic transport regime the solids are equally distributed over the riser height indicated by a nearly constant pressure decay along height. The pressure profile of the FR shows the typical shape of a CFB while the profile in the AR had a shape similar to the one of a pneumatic conveyor. This occurs because of the relatively low gas velocity in the FR and the high gas velocity and low solids inventory in the AR. In the DCFB concept three loop seals are needed. Proper operating loop seals show a pressure drop in solids flow direction indicating movement of solids and appropriate gas sealing. Operation stability of loop seals towards pressure fluctuations between the loop seal inlet and outlet can be obtained by increasing the pressure at the bottom of the loop seal. In the DCFB concept the lower and upper loop seal are directly exposed to fluctuations and differences of pressure between the two fluidized beds. For that reason deeper loop seals will improve the operation stability of the system.

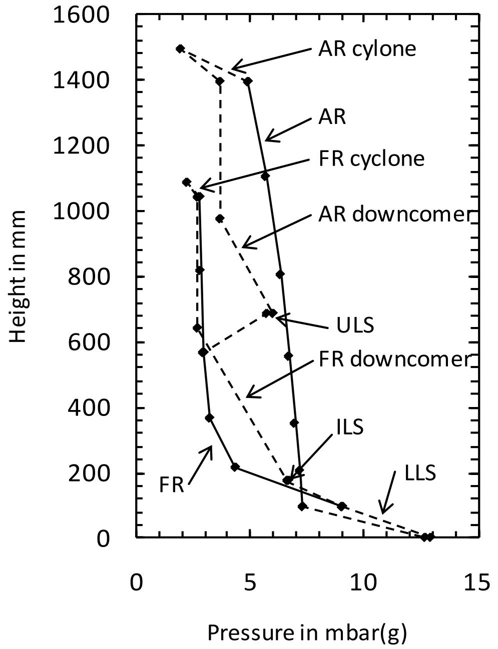

Fig. 4 Typical pressure profile of the CFM with 0.5 kg total inventory and at following fluidization rates in Nm^3/h: AR 25/FR 5/LLS 0.5 ULS 0.6/ILS 0.2

Impact of gas velocity

To study the effect of the AR fluidization the gas volumetric flow to the AR was varied at constant FR and loop seal fluidization. Pressure profiles are shown in Fig. 5. With increasing gas flow rate to the AR it was observed that the overall pressure profiles were shifted towards a higher pressure which was caused by increased back pressure from the filter bag and cyclone. It was also observed that although the pressure profile of the AR was affected by gas velocity in the AR the FR profile itself remained nearly unchanged. Inaccurate pressure probe placement was detected at the bottom of the AR showing a discrepancy from the expected pressure profile. Rearrangement of the probe has to be considered in further investigations.

Results of solids circulation rate measurement are depicted in Fig. 6. At low flow rates of 20 to 30 Nm^3/h in the AR an increasing solids flux was observed while at high fluidization velocities the solids flux decreased. This is in contrast to the expected behavior that the solids circulation rate increases with fluidization rate.

One reason for this seems to be that the increasing back pressure from the filter bag with AR fluidization rate is affecting the actual solids inventory in the AR. It might also be that due to the fact that the fluidization nozzles of the AR are inclined downwards (Fig. 3) the dynamic pressure of the gas flow increases the back pressure at the outlet side of the lower loop seal, thus inhibiting solids flow. Fig. 6 also shows that the AR fluidization rate has only a minor effect on the FR internal solids circulation rate which is in agreement with the observed pressure profiles and previous investigations (13).

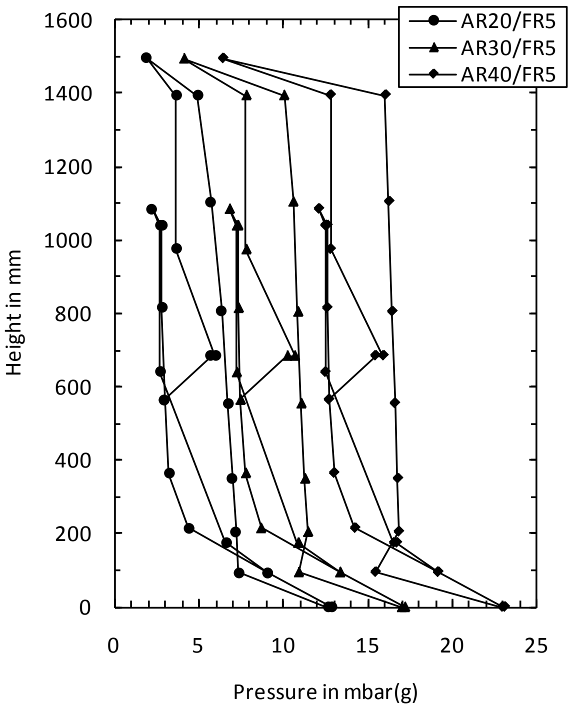

Fig. 5 Influence of AR fluidization on the pressure profile at a total solids inventory of 0.5 kg and following fluidization rates in Nm³/h: FR 5/ ULS 0.5/LLS 0.5/ILS 0.2

Impact of reactor outlet pressure difference

To study the effect of reactor outlet pressure difference the FR backpressure was changed by closing or opening a valve placed after the dip tube of the FR cyclone. The CFM results are shown in Fig. 7. It was found that with increasing pressure difference the AR solids entrainment rate increased nearly linearly with the pressure difference while the FR internal

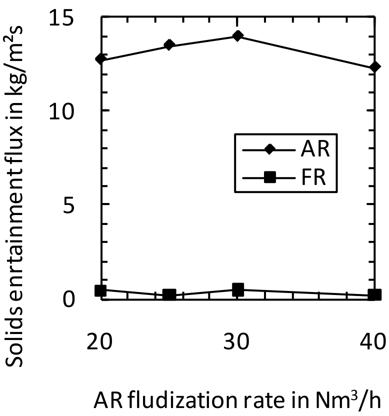

Fig. 6 Influence of the AR fluidization on the solids circulation relative to reactor cross-section at a total inventory of 0.5kg and the following fluidization rates in Nm³/h: FR 5/ULS 0.5/LLS 0.5/ ILS 0.2

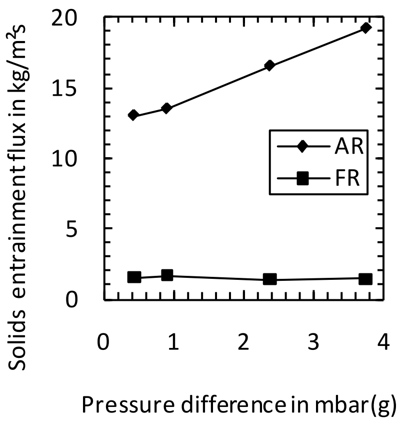

Fig. 7 Influence of the riser outlet pressure difference on the solids circulation relative to riser cross-section at a total inventory of 0.5kg and the following fluidization rates in Nm³/h: AR 25/FR 5/ULS 0.5 / LLS 0.5/ILS 0.2

circulation rate remained unaffected. This can be explained by the increased driving force for particle movement through the lower loop seal which is governed in the DCFB concept by the solids inside the riser of the fuel reactor and the back pressure from the fuel reactor exhaust line. It is important to note that when the pressure difference between the risers is increased too far, solids accumulation in the downcomer of the AR cyclone can lead to loop seal blockage by occurrence of a slugging fluidized bed regime in the downcomer. On the other hand also emptying of the upper loop seal can occur at inversed pressure differences. Generally, in pressurized conditions, small relative backpressure changes can cause significant changes in solids circulation and possibly lead to failure of loop seal operation. Deep loop seals better resisting pressure difference fluctuations between loop seal inlet and outlet can be part of a solution. In addition it seems that an automatic backpressure control setup is inevitable for pressurized operation of a DCFB.

CONCLUSIONS

The chemical looping reforming process for autothermal steam reforming has shown great potential at atmospheric conditions. To minimize the compression work needed a key issue is to operate the process under pressurized conditions. Pressurization influences the process from the chemical-, as well as from the hydrodynamic point of view. Because of increased gas density the reactor cross section area decreases resulting in increased gas-solids reaction intensity. To avoid occurrence of critical solids flux values in the AR riser recycling of parts of the AR off-gas is needed. This recycling gas stream should be kept low to decrease the energy penalty from re-heating the recycle-gas. This has to be considered when aiming for high process temperatures to improve the methane conversion.

Possible problems occurring at pressurized operation were indentified in a dual circulating fluidized bed cold flow model. Proper operation of the loop seals placed between the two risers requires controlling the pressure difference between the reactors. High solids throughput and high pressure differences might lead to loop seal feeding tube blockage or emptying of the loop seal. A pressurized system will therefore be characterized by loop seals larger in both cross section and depth. It was also found that increasing the back pressure of the FR increases the global solids circulation rate which might be used to control the solids circulation rate between the air reactor and the fuel reactor.

NOTATION

AR	Air reactor	CFB	Circulating fluidized bed
CFM	Cold flow model	CLC	Chemical looping combustion
CLR	Chemical looping reforming	D	Bed diameter, mm
DCFB	Dual circulating fluidized bed	DFB	Dual fluidized bed
d_p	Particle mean Sauter diameter, μm	FR	Fuel reactor
g	Gravitation constant, m/s²	htx	Heat exchanger
ILS	Internal loop seal	LLS	Lower loop seal
MeO	Metal oxide	OC	Oxygen carrier
PCLR	Pressurized chemical looping reforming	U_0	Superficial gas velocity, m/s

ULS	Upper loop seal	$\Delta H_R^{900°C}$	Reaction enthalpy at 900°C, kJ/mol
η_g	Gas viscosity, Pa·s	ρ_g	Gas density, kg/m³
ρ_p	Particle density, kg/m³	Ψ	Sphericity, -

REFERENCES

1. Bellona Report 6:02. Bellona Foundation 2002.

2. Dybkjaer I.: Fuel Processing Technology 42 (April 1995) 85-107.

3. Lyngfelt A., Johansson M., Mattisson T., CFB Technology IX. Hamburg, Germany: TuTech; 2008.

4. Hossain M.M., de Lasa HI., Chem. Eng. Sci. 63 (2008) 4433-4451.

5. Johansson M., Mattisson T., Rydén M., Lyngfelt A., International Seminar on Carbon Sequestration and Climate Change, Rio de Janeiro, October 2006.

6. Linderholm C., Mattisson T., Lyngfelt A., Fuel 88 (2009) 2083-2096.

7. Kolbitsch P., Pröll T., Bolhàr-Nordenkampf J., Hofbauer H., Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC., November 2008.

8. Lynfelt A., Leckner B., Mattisson T., Chem. Eng. Sci. 56 (2001) 3101-3113.

9. Kolbitsch P., Bolhàr-Nordenkampf J., Pröll T., Hofbauer H., Chem. Eng. Sci 32 (3) (2009) 398-403.

10. Rydén M., Lyngfelt A., Mattisson T., Energy & Fuels 22 (2008) 2585-2597.

11. Pröll T., Bolhàr-Nordenkampf J., Kolbitsch P., Marx K., Hofbauer H., Proceedings of the 2009 AIChE Spring National Meeting and 5th Global Congress on Process Safety, Tampa, FL, April 26-30, 2009.

12. de Diego LF., Gayán P., Adánez J., Abad A., Dueso C., Ind. Eng. Chem. Res. 48 (2009) 2499-508.

13. Pröll T., Rupanovits K., Kolbitsch P., Bolhàr-Nordenkampf J., Hofbauer H., Chem. Eng. Technol. 32 (2009) 418-424.

14. L. R. Glicksman, Chem. Eng. Sci. 39 (1984) 1373-1379.