

Chemical looping combustion for industrial steam generation from natural gas with inherent CO₂ capture

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Abstract

The concept of a 300MW steam production plant for heavy oil extraction by chemical looping combustion (CLC) was evaluated. The reactor design bases on the dual circulating fluidized bed (DCFB) design of the 120kW pilot plant at Vienna University of Technology. Expected performance of such a plant is calculated when CO₂ purification is included. It is shown that CLC could be used for large scale steam production including carbon capture with practically very little energy penalty. Thermal efficiencies of about 90% can be expected while carbon dioxide is captured quantitatively. Thus, steam production is an ideal application for CLC whenever carbon capture is needed.

Keywords: chemical looping combustion, CLC, design study, CCS, carbon capture

Introduction

Rising carbon dioxide concentration in the atmosphere has become more and more the focus of investigation in recent years. It is well agreed among most scientists that CO₂ emitted from anthropogenic sources contributes to the greenhouse gas effect. Thus, these gases play a significant role when it comes to global warming. The key midterm strategy to reduce the anthropogenic greenhouse gas emission is carbon capture and storage (CCS) [1]; where the CO₂ is separated from combustion processes, compressed and sent to storage locations. Chemical looping combustion (CLC) is a promising and low cost technology for CO₂ capture.

In general a chemical looping process consists of two separate reactors; an air (AR) and a fuel reactor (FR). A solid metal oxide is circulated between these two zones used to transport oxygen and heat from the AR to the FR. The metal oxide is therefore often also called oxygen carrier (OC). In the AR, the OC entering is contacted with ambient air where they are oxidized. The gas leaving the AR therefore is simply oxygen depleted air and can be released to the surrounding without major concerns. The fuel and the oxidized oxygen carrier are fed to the FR where the OC releases oxygen in interaction with the input fuel. The reduced OC is then recycled back to the AR where the loop starts again. The FR outlet gas consists predominantly of CO₂ and water vapor, depicted in Fig. 1.

Compared to oxyfuel with CLC the oxygen is supplied by the OC without an air separation plant. Compared with post combustion CO₂ capture, no gas-gas separation is needed because the fuel is not in direct contact with atmospheric nitrogen. This is why the energy penalty for carbon capture using CLC is much lower than in other CO₂ capture processes. The potential of CLC for gaseous fuels at atmospheric conditions has been demonstrated in the past in a large number of laboratory and pilot plant facilities ([2], [3]). Next step in evolution of the process would be the scale up to industrial sizes. This will need an integration of the process into a power or heat generation system.

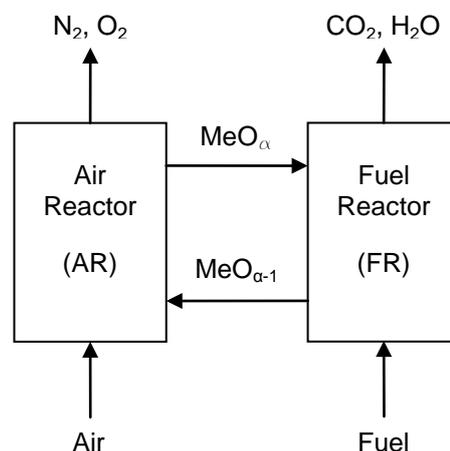


Fig. 1 Chemical looping combustion principle

Nowadays, the process of choice for power generation from gaseous fuels is the natural gas combined cycle (NGCC) where thermal efficiencies of up to 60% [4] are obtained. Caused by the relative low process temperature in atmospheric CLC thermodynamically this thermal efficiency is out of CLC's range. Pressurization will make the difference but is currently not realistic because a lot of research will be necessary. A lot of industrial processes, such as paper production, require steam. Usually small scale natural gas fired once-through steam generators are used. Though in CLC CO₂ is separated the efficiency is in a comparable range to such once-through boilers ([5],[6]). Heavy oil extraction from in situ oil sands where steam is injected to reduce the oil viscosity is considered a promising application for CLC [7]. In this study the design of such a 300 MW steam production plant using CLC is carried out. It is based on the dual circulating fluidized bed (DCFB) developed for chemical looping processes at Vienna University of Technology [8]. Heat recovery and CO₂ compression and purification are considered and efficiencies are calculated by mass and energy balance investigations.

Governing reactions

The main reaction occurring in the air reactor is the oxidation of the oxygen carrier with ambient air.



The situation inside the FR is more complex governed by many reactions taking place in parallel or in sequence. In the case of nickel based oxygen carriers it is very likely that catalytic activated steam reforming and CO-shift are occurring at relevant magnitude.



Consecutively oxidation of reformed products with the oxygen carrier occurs.



Complete combustion of the fuel is formally represented by reactions (2) & (5). While the OC oxidation reaction inside the AR is always strongly exothermic the oxidation of the fuel can be endo- as well as slightly exothermic depending on the oxygen carrier and the fuel used [2]. Nevertheless, the global heat release is the same as in combustion with ambient air which can be derived by combining reactions (1) to (5).

Definition of relevant quantities

To characterize the potential of CLC to convert fuel the so called fuel conversion and CO₂ yield are defined. For methane as fuel they are:

$$X_{\text{CH}_4} = \frac{y_{\text{CO}} + y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{CH}_4}} \Bigg|_{\text{FRout}} \quad (6)$$

$$Y_{\text{CO}_2} = \frac{y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{CH}_4}} \Bigg|_{\text{FRout}} \quad (7)$$

While the fuel conversion indicates the amount of remaining fuel in the FR off-gas the CO₂ yield describes the extent to which fuel is fully oxidized to CO₂. High fuel conversion and CO₂ yield are therefore beneficial in CLC.

An important parameter in CLC is the global stoichiometric air/fuel ratio defined as:

$$\lambda = \frac{O_2|_{AR,in}}{O_2|_{FR,required}} \quad (8)$$

It indicates the available oxygen at the AR inlet to the oxygen needed for full combustion of the fuel provided to the FR. In CLC where full conversion of the fuel is intended lambda is in general above one.

Oxygen carrier (OC) characterization

The basic requirements for oxygen carriers are mechanical stability, lowest possible costs and high oxygen transport capacity. Depending on the fuel used, the oxygen carrier has to fulfill other requirements too. For hydrocarbon fuels a high catalytic activity is beneficial. Nickel-based carriers are highly catalytically active and therefore suitable for methane combustion and reforming. Other possible metals besides Ni are: Cu, Fe, Co, Mn, and Cd. A comprehensive overview can be found in [10]. Most oxides have to be supported by other inert materials to gain the necessary mechanical strength and attrition resistance to be operated in CLC. Such support materials can be Al_2O_3 , TiO_2 , or yttria-stabilized zirconia (YSZ) [5].

In the present study, the OC consists of NiO supported on $\alpha-Al_2O_3$, and MgO. These particles have shown great potential towards fuel conversion in experiments at the 120kW pilot [11] where methane conversions of over 99% have been achieved. The particle size of the oxygen carrier is in the range of 90 to 210 μm and with a Sauter mean diameter of 119 μm typical for circulating fluidized bed applications. The OC characteristics are summarized in Table 1. Additional information on the oxygen carrier is reported in [12].

Table 1 Oxygen carrier characterization

Notation	Symbol	Value	Unit
RedOx system		Ni/NiO	-
Support materials		Al_2O_3+MgO	-
Active Ni content		41.3	wt%
Oxygen transport capacity	R_0	0.087	kg/kg
Sauter mean particle diameter	d_p	119	μm
Particle density	ρ_p	3200	kg/m ³
Sphericity	ψ	0.9	-
Voidage at minimum fluidization	ϵ_{mf}	0.4	-

Fluidized bed system design

In CLC it is required that:

- The global solids circulation rate between the air and fuel reactor has to be sufficient to ensure oxygen transport and to reduce the temperature difference between the reactors.
- The gas-solids contact in both reactors must be maximized for high fuel conversion.

Dual fluidized bed systems have been successfully applied to the chemical looping process in the past to meet CLC requirements ([5], [8]). Most of the systems consist of an AR operated in circulating fluidized bed regime while the FR is designed to operate in bubbling or in turbulent fluidized bed regime. Bubbling fluidized beds (BFB) suffer from the disadvantage of gas bypass through the bubble phase without sufficient solids contact, leaving the reactor practically unconverted. In general also the cross-section area and solids inventory of BFB are much higher than in a CFB which is particularly important when expensive oxygen carriers, .e.g. nickel based ones, are used. Furthermore in the practically particle-free freeboard of a BFB no gas-solids reactions are likely to occur. In a CFB gas-solids contact is increased with solids present over the whole reactor height. For that reason the so called dual circulating fluidized bed (DCFB) reactor system for CLC has been developed at Vienna University of Technology [8].

The design of the DCFB consists of two interconnected circulating fluidized beds. Loop seals between the reactors fluidized with superheated steam connect the reactors and avoid mixing of AR and FR gases. Downstream of each reactor, gas and solids are separated in cyclones. The general setup is shown in Fig. 2. The system includes two solids loops. One loop, the global loop, is the solids loop closed by the AR, and the upper and lower loop seal. The second loop is the FR internal loop closed via the FR and the internal loop seal. Ideally the two loops are independent of each other allowing the FR to be operated independently resulting in complete fuel conversion. More specific details about the DCFB system can be found elsewhere [8].

Air reactor design

The global solids circulation rate in the DCFB design is determined mainly by the AR. To decrease the temperature difference between the reactors high circulation rates are beneficial. Therefore the AR is designed as a fast fluidized bed. The onset of fast fluidization is described as the regime where significant solids entrainment from a lower dense section of the fluidized bed is observed. Bi and Grace [13] addressed this limit as the superficial velocity U_{se} which is calculated with the corresponding Reynolds number, Re_{se} , as:

$$Re_{se} = 1.53 \cdot Ar^{0.50} \quad (2 < Ar < 4 \cdot 10^6) \quad (9)$$

For proper operation over a wide operation range the AR superficial gas velocity range is:

$$U_{AR} = 7 - 8 \frac{m}{s} \quad (10)$$

This value corresponds to approximately 1.5 times of U_{se} for the chosen OC.

Fuel reactor design

The main design criterion of the FR is to maximize the gas-solids contact while keeping the solids inventory low. Turbulent fluidized beds are characterized by bubbles break-up instead of bubble growth like in bubbling bed. Small voids and particle cluster darts to and from the indistinct top surface of the bed. Thus, potential gas-slip through the bubble phase is minimized while gas-solids contact is expected to increase. The onset of turbulent regime is defined by the critical velocity U_c where standard deviation of the pressure fluctuation reaches a maximum. It is believed that this point reflects a dynamic balance between bubble coalescence and break-up. The turbulent regime according to Bi and Grace [13] is defined by the velocity range from U_c to U_{se} , with U_c calculated from:

$$Re_c = 1.24 \cdot Ar^{0.45} \quad (2 < Ar < 1 \cdot 10^8) \quad (11)$$

The FR design superficial gas velocity is chosen to be in the middle of the turbulent regime. The FR superficial gas velocity range is:

$$U_{FR} = 4.5 - 5.5 \frac{m}{s} \quad (12)$$

The design operation points of the air and fuel reactor are shown in the flow regime map suggested by Bi and Grace [13] in Fig. 3.

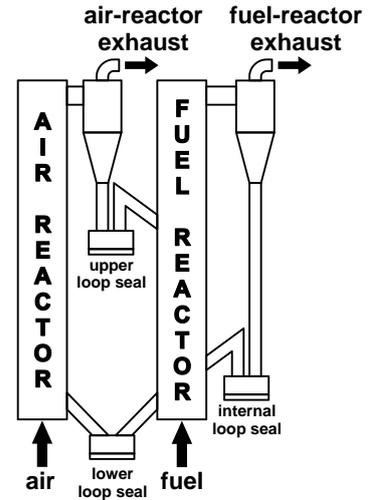


Fig. 2 Sketch of the DCFB system

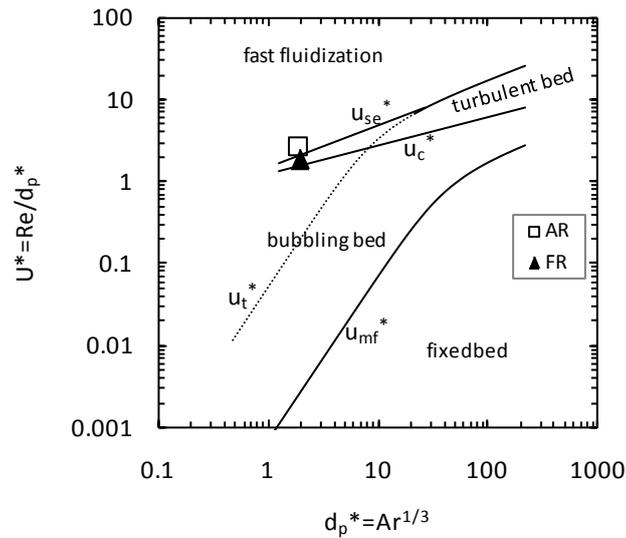


Fig. 3 Fluidization regime of the air and fuel reactor in the flow regime map suggested by Bi and Grace [13]. The fuel reactor is operated in turbulent and the air reactor in fast fluidization regime.

Heat integration

In thermal processes heat integration is important to ensure proper energy conversion. In CLC the cooling system is also needed to control the reactor temperatures. Practically two limits occur. Elevated temperature is required for high fuel conversion depending on the reactivity of the OC. On the other hand the OC maximum temperature is limited by occurrence of agglomeration and attrition of the particles. Thus, the system has to operate in a temperature range where the reaction rates are high enough while still sufficient OC mechanical stability is ensured. CLC reactions will already take place at relative low temperature such as 750°C in the FR but good fuel conversions have been observed at a fuel reactor temperature of approximately 900°C [11]. Thus, the fuel reactor design temperature range is chosen to be:

$$T_{FR} = 900^{\circ}C \quad (13)$$

Where a methane conversion performance and a carbon dioxide yield of

$$X_{CH_4} = 99.39\% \quad (14)$$

$$Y_{CO_2} = 92.20\% \quad (15)$$

have been observed in the 120 kW pilot rig at Vienna University of Technology [11]. To limit the temperature of the reactors the system can be cooled by:

- increasing the amount of excess air in the air reactor, or by
- cooling the reactor casing, or by
- using bed material coolers.

Increasing the excess air increases the loss of sensible heat with the gas leaving the heat recovery section resulting in an efficiency loss. In addition the reactor cross-section area increases proportionally with gas flow. For that reason this option seems to be impractical. Cooling the reactor by use of water walls and bed material coolers is widely used in industrial circulating fluidized bed applications. Both options can be used independently but a combination of both seems to be the most viable.

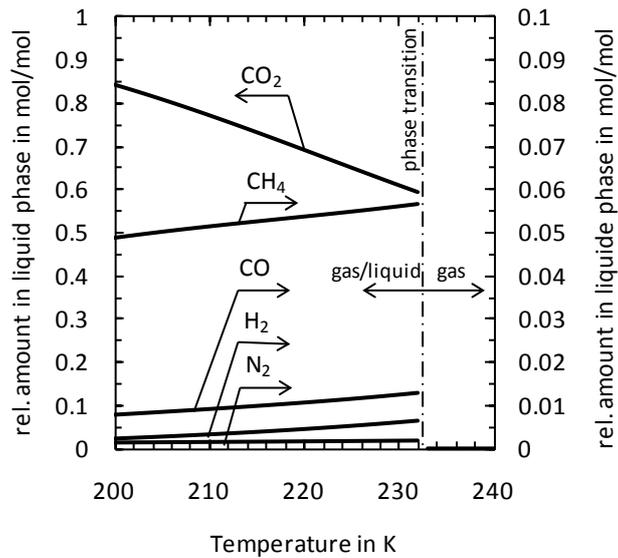


Fig. 5 Relative gas components solubility in liquid CO₂ depending on temperature at a pressure of 15 bar(a) and the following raw-gas composition in mol%: CO₂ 70 / CH₄ 7.5 / CO 7.5 / H₂ 7.5 / N₂ 7.5. Property data taken from GERG-2004 XT wide range equation of state.

Expected overall performance

In chemical looping gases and solids have to be considered simultaneously. Most of commercial available mass and energy balance tools do not yet offer this possibility. Bolhar-Nordenkampf et al. [14] present the so-called advanced energy technology library (AET-Lib), which is an extended version of a comprehensive model library previously built for gasification-based processes [15]. The library includes 40 substances potentially involved in chemical looping. The library in combination with the commercial available solver IPSEpro is used and a numerical model of the chemical looping process has been implemented into the environment. The model was validated by empirical measurements of the 120 kW pilot at Vienna University of Technology. This model was used in the design of the 300 MW CLC plant. Heat recovery, blowers, auxiliary steam (for loop seal fluidization) and the recycle stream from the cryogenic CO₂ purification unit are considered. The main basic design parameters are summarized in Table 2. Natural gas mainly composed of methane (97 vol%) is used.

Table 2 Basic design parameters

Item	Value	Unit
Thermal steam power output	300	MW
Steam pressure	100	bar(a)
Steam quality	100	%steam
Fuel	Methane	-
Global air/fuel ratio	1.1	-
Methane conversion	99.2 to 99.6	%
CO ₂ yield	92.0 to 92.4	%
Mean oxygen carrier oxidation state	30	%
AR rectangular cross-section	55 to 60	m ²
FR rectangular cross-section	28 to 30	m ²

In this design a thermal efficiency of nearly 90 % is possible while large quantities (99 wt%) of the input fuel carbon is captured. Only minor additional energy is needed in the process. Expected performance data and basic design results are summarized in Table 3.

Table 3 Expectable performance and basic design results

Item	Value	Unit
Required fuel power	330 to 338	MW
Secondary steam demand	3.5 to 3.9	MW
Auxiliary units electrical power demand (CO ₂ compression not included)	4.6 to 5.0	MW
Carbon recovery rate	99	wt%
Air reactor outlet superficial gas velocity	7.2 to 7.6	m/s
Fuel reactor outlet superficial gas velocity	5.0 to 5.4	m/s
Expected air reactor pressure drop	200	mbar
Expected fuel reactor pressure drop	180	mbar

Conclusions

A chemical looping process (CLC) based on nickel oxides as oxygen carrier and natural gas as fuel was applied to a conceptual steam production plant of 300MW for heavy oil recovery. The reactor design was based on the dual circulating fluidized bed design of the 120 kW pilot at Vienna University of Technology. The reactor system was designed and a heat recovery system was proposed. CO₂ purification techniques were assessed and put into consideration. It is shown here that CLC could be used for large scale steam production including carbon capture with very low energy penalty. Thermal efficiencies of about 90% could be expected while about 99 % of the carbon in the input fuel could be captured. Thus, steam production is an ideal application for CLC whenever CCS is needed.

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Notation

AR	air reactor	R_0	oxygen transport capacity, kg/kg
BFB	bubbling fluidized bed	X_{CH_4}	methane conversion, -
CFB	circulating fluidized bed	Y_{CO_2}	carbon dioxide yield, -
CLC	chemical looping combustion	y_i	fraction of species i, -
CLR	chemical looping reforming	ε_{mf}	voidage at minimum fluidization, -
d_p	sauter mean particle diameter, μm	λ	air/fuel ratio, -
FR	fuel reactor	ρ_p	particle density, kg/m ³
MeO	metal oxide	ψ	sphericity, -
OC	oxygen carrier		

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