Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

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Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1
D.C. Thomas and S.M. Benson (Eds.)

Chapter 37

CHEMICAL LOOPING COMBUSTION OF REFINERY FUEL GAS WITH CO_2 CAPTURE

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ABSTRACT

Chemical looping combustion (CLC) is a new combustion technology with inherent separation of CO_2. Metal oxides are circulating between two fluid bed reactors: a fuel reactor for fuel oxidation and an air reactor for metal oxides oxidation by contact with air. The combustion products CO_2 and H_2O are obtained in a stream separate from oxygen depleted air stream.

Alstom Power Boilers has developed a design concept for a large-scale Chemical Looping Combustion boiler (200 MWth refinery gas in Grangemouth) using modified circulating fluidized bed (CFB) technology with fluid bed heat exchangers. No hard point appears in terms of technology except metal oxide durability needs to be confirmed. Preliminary economics suggest that for a 200 MWth CLC gas fired CFB boiler CO_2 mitigation costs could be among the lowest for the technologies so far screened by the CCP. Detailed economics are currently being developed for alignment with other technology option costs reported by the CCP common economic modeling team (CEM) during the course of the 2003/2004 development project.

CLC technology for refinery and natural gas combustion using CFB boilers might appear as a leading technology in term of competitiveness for CO_2 removal and quick access to the market after a long-term prototype operation and a demonstration unit operation.

CHEMICAL LOOPING COMBUSTION PRINCIPLE

Chemical looping combustion is a relatively new technology, which integrates air separation into the combustion process and produces a separate CO_2/H_2O flue gas stream for CO_2 capture. The principle is to separate the fuel oxidation process from the air stream by carrying oxygen to the fuel in the form of a metal oxide. In oxidizing the fuel in a “fuel reactor”, the metal oxide is reduced and then transported to an “air reactor” where it is re-oxidized by contact with air, leaving an oxygen-depleted air stream. The oxide is then returned to the fuel reactor. The scheme is illustrated in Figure 1.

CONVENTIONAL CIRCULATING FLUIDIZED BED TECHNOLOGY

The basic process principle of a CFB boiler is to perform solid fuel combustion in a high inventory fluidized bed where the solid fuel and the sorbent are recycled many times. The low temperature, long fuel residence time and high combustion efficiency inherent in the process result in 0.low emissions and the ability to burn any solid fuel [1].

For conventional applications of coal fired power plants without CO_2 capture, circulating fluidized bed (CFB) technology has demonstrated an unparalleled ability to achieve low SO_2 and low NO_x emissions without the need for back-end equipment such as selective catalytic reduction system. This is possible due to low combustion temperatures (830–900 °C) and the staging of air.

Abbreviations: CFB, Circulating fluidized bed; FBHE, Fluidized bed heat exchanger; CLC, Chemical looping combustion.

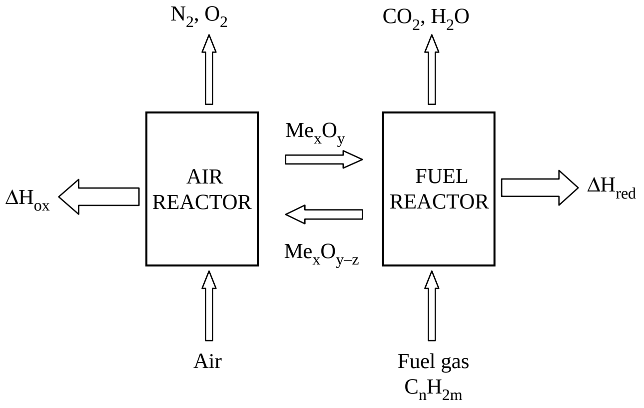

Figure 1: Principle of chemical looping combustion (Me_xO_y = metal oxide).

Currently, based on its demonstrated scale-up ease, low emissions capabilities and fuel flexibility, CFB technology is a serious option for many applications in mid-sized (300–450 MWe) and larger (400–600 MWe) utility unit applications.

Typical CFB Boiler Layout

A typical CFB boiler loop (Figure 2) features a single water wall cooled furnace, with a refractory lined bottom, cyclone separators, and external fluidized bed heat exchangers (FBHE), for furnace temperature control containing the medium temperature superheaters and for reheat steam temperature control containing the finishing reheaters. This design avoids the use of spray water for final reheat temperature control and improves the cycle efficiency. The flow of solids passing through each FBHE is regulated automatically by a water-cooled ash control valve, whereas the balance of solids is re-circulated to the bottom of the furnace through seal pots. The pressure parts not enclosed in the solid loop are located in a traditional convective backpass linked to the cyclones by two large flue gas ducts.

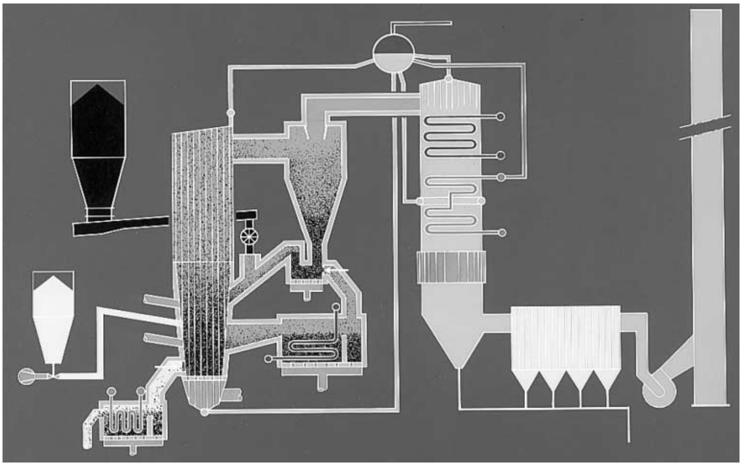

Figure 2: Circulating fluidized bed boiler with fluid bed heat exchanger.

Combustion Process

Fuel is injected in the ducts downstream of the seal pots to ensure an homogeneous distribution of the fuel in the furnace. Primary air is injected through a grid of special fluidizing air nozzles located at the bottom of the furnace. The role of the primary air is to lift the bed of particles and to fluidize it. Secondary air is injected through numerous ports at two levels above the grid in order to stage and distribute this injection. The role of the secondary air is to ensure the strong agitation of the particles as well as their mixing necessary to the process. The ratio of primary to secondary air has a strong influence on NO_x emissions and on upper furnace solids concentration directly related to the heat transfer coefficient. Fluidizing air is also injected in the FBHEs and seal pots.

Careful consideration is given to the geometry of the combustor as this impacts air and fuel mixing. The lower furnace design enables the air and fuel particles to mix in an area that is roughly one-half of the overall combustor plan area.

Typical combustion temperatures of 830/900 °C are the optimum in respect to inherent sulfur capture, limestone consumption and NO_x emissions.

Sulfur capture is achieved through inherent capture by the fuel bound calcium when available and by injection of prepared and dried limestone in the furnace. Sulfur capture efficiency as well as NO_x emissions vary greatly with bed temperature; therefore, the ability to control such temperature with FBHEs is a key advantage.

Separation System

The cyclone sizing and geometry, which includes the design of the inlet duct, is at the heart of ALSTOM Power Boilers CFB combustion technology—the capture efficiency of the separation system is the decisive factor in maintaining the bed density, retaining the fine particles in the loop, particularly the fine, calcium-rich particles. A high bed density in turn ensures a high heat transfer and an homogeneous temperature in the furnace, a high contact between CaO particles and SO_2-rich flue gas for optimum sulfur capture efficiency and of course the best possible combustion by keeping the fuel particles in the furnace for the longest possible time. It also has a beneficial impact on NO_x emissions.

CHEMICAL LOOPING COMBUSTION—INDUSTRIAL CONCEPT

ALSTOM Power Boilers has developed a design concept for large-scale Chemical Looping Combustion boiler (200 MWth refinery gas boiler in Grangemouth) using existing CFB technology with fluid bed heat exchangers.

Novel design criteria for the heat and mass balance of the CLC boiler, considering simultaneously the oxygen need for fuel conversion and solids enthalpy need for oxygen carrier oxidation/reduction had to be satisfied, with integration of hot prototype tests data.

The heart of the CLC combustion plant is an interconnected air reactor and fuel reactor using fluid bed technology. The air reactor is a conventional CFB while the fuel reactor is a bubbling bed. The fuel, refinery gas in this case, is introduced into the fuel reactor as fluidization gas where it is oxidized by the oxygen carrier, metal oxide (MeO). The exit gas from the fuel reactor contains CO_2 and H_2O and almost pure CO_2 is obtained when H_2O is condensed. Particles of the oxygen carrier are transferred to the air reactor where they are regenerated by contact with air. Flue gas at air reactor outlet is composed of N_2 and some unused O_2.

The total amount of heat involved is the same as for normal combustion. The key advantage is that the CO_2 is not diluted with N_2.

During the design, the particle size distribution of the oxygen carrier has been assessed concerning its compatibility with large-scale industrial cyclone and with required solids loading for feeding the fuel reactor. This compatibility is the key for proper operation of CLC loop. Since there is an optimum temperature range for the oxides operation, load follow-up requires a close temperature control of the air riser loop, which has led to the installation of a fluid bed heat exchanger which allows to adjust the heat duty removed from the solids loop. The need of secondary air injection in the air reactor to adjust the solids recirculation rate, typical practice in conventional CFB has been reconducted to allow the adjustment of the upper solids concentration which is directly related to the heat transfer coefficient in the upper air reactor.

Another novel aspect is the air reactor loopseal with three solids outlets: direct return to the air reactor, controlled extraction to FBHE and to fuel reactor using two solids flow control valves. The Chemical Looping Boiler concept from ALSTOM Power Boilers provides solutions for gas barriers between fuel reactor and the air reactor which is crucial for the interconnected reactors performances. Finally, the split backpass for two separate gas streams is quite similar to existing practice for reheat control.

Chemical looping combustion (CLC) of refinery fuel gas (Figure 3) shares equivalent challenges with CFB technology, since:

- the air reactor being the equivalent of the combustor;
- the cyclones playing similar duties, with even higher performances requirements, resulting from the high solids flow rate;
- the backpass playing similar duties;
- the FBHE playing similar duties;
- the fuel reactor is a bubbling bed quite similar to FBHE.

Air Reactor

For CLC using CFB technology, oxide conversion and the heat transfer to the combustor walls and in-combustor surface are a result of fluidization of the bed. The location of the secondary air along the front and rear walls creates conditions to control the upper combustor solid loadings and external solids circulation to the FBHE and fuel reactor.

Cyclones

For CLC using CFB technology, cyclones separate the entrained oxide particles from the oxygen depleted air leaving the air reactor. The efficiency of the cyclone impacts the capture rate of the fines fraction of the oxides entering the cyclone. This in turn affects the allowable oxide particle size distribution which should be as finer as possible for heat and mass transfer purposes.

Fluid Bed Heat Exchanger

For CLC using CFB technology, FBHE have similar heat duties of cooling recirculated oxides coming from the cyclones, before reinjection in the air reactor bottom. Both the higher particle density and the need to maximize the heat transfer coefficient leads to higher fluidizing velocity for CLC case.

Fuel reactor

For CLC using CFB technology, fuel reactors are a new feature, but using similar turbulent fluid bed conditions with high fines recirculation resulting from high efficiency cyclones located above the fuel reactor and built with a mechanical construction similar to FBHE. The novelty is the fuel gas fluidization system which is particular since it is using a distributed nozzles system, instead of a large windbox, which might be hazardous.

Backpass

A specific feature of the backpass for chemical looping CFB application, differing from the conventional CFB, is the two channels of flue gas cooling, one stream of CO_2/H_2O and the other stream of oxygen depleted air. Complete tightness between the two channels is required to avoid CO_2 stream dilution by oxygen depleted air.

SCALE-UP ISSUES FOR CHEMICAL LOOPING CFB

The major scale-up technical challenges are with three major components of CFBs: the combustor, the cyclones, and the fluid bed heat exchangers [2].

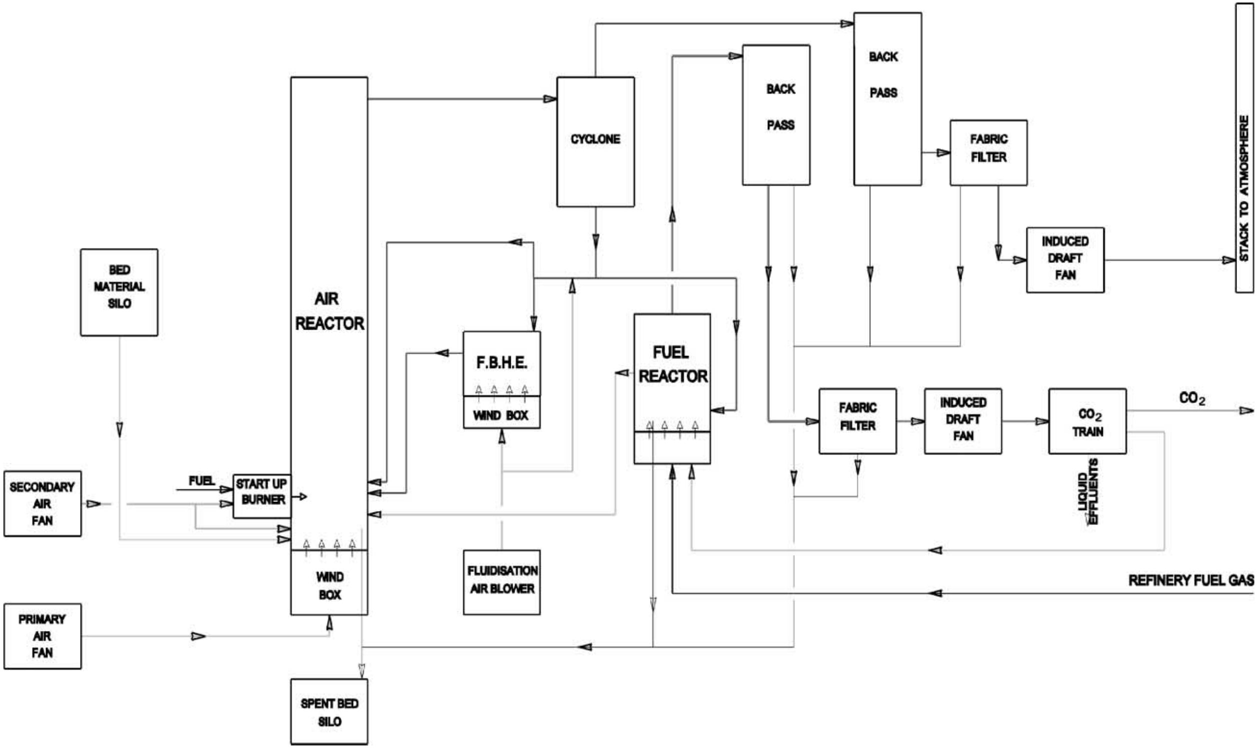

Figure 3: Chemical looping combustion CFB.

Combustor

For general scaling-up of CFB design from existing units, ALSTOM Power Boilers increases the combustor height only slightly to ensure the solids pressure profile, and therefore, heat transfer to the waterwalls is within our proven experience and knowledge base [3].

As the unit size increases, the depth of the unit remains constant to ensure good mixing of air and oxides in the lower furnace. The width of the unit increases and cyclones are added as required to maintain gas velocities at optimum levels. As units increase in size to a point where four (4) cyclones are required, the combustor bottom design changes to a pant-leg. This offers the possibility to implement mid-walls heat exchangers above the pant-leg up to the furnace roof.

Cyclones

In scaling-up, a point is reached where the cyclone size gets so large that the oxygen carrier particles losses increase significantly. Scale-up to larger size cyclones has been gradual.

Like for conventional CFB, as the unit size increases, cyclone size is increased or cyclones are added as required to maintain optimum gas velocities, and then optimum cyclone fractional collection efficiency.

Since approximately 75% of the gas flows through the air reactor cyclones, the air reactor cyclones have the following arrangements (Figure 4):

- 1 cyclone up to 135 MWe;
- 2 cyclones between 135 and 270 MWe;
- 3 cyclones between 270 and 400 MWe;
- 4 cyclones between 400 and 540 MWe;
- 6 cyclones above.

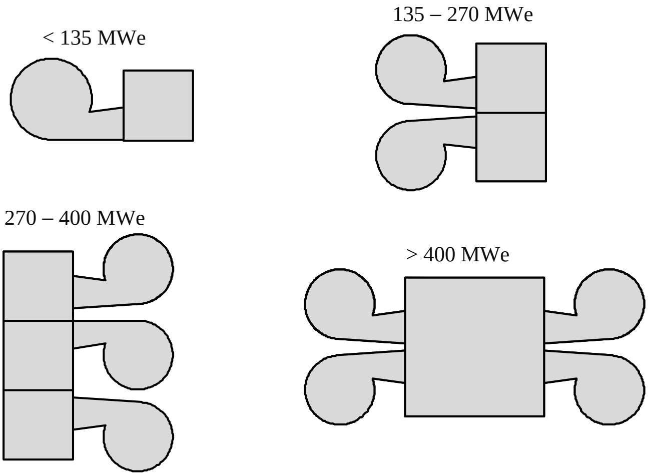

Figure 4: Typical cyclone arrangement.

FBHE

As CFBs get larger in size, the combustor surface-to-volume ratio decreases with a simultaneously increasing share of FBHE heat duty. The FBHEs allow incremental heat duty by passing a sufficient amount of recycle solids into the bundles (Figure 5). An inherent benefit of using a FBHE is the relatively high heat transfer rate from the hot solids to the tube bundles. By standardizing tube bundle arrangements and by utilizing a modular approach, an increase in unit size can be accommodated without developing new FBHE designs.

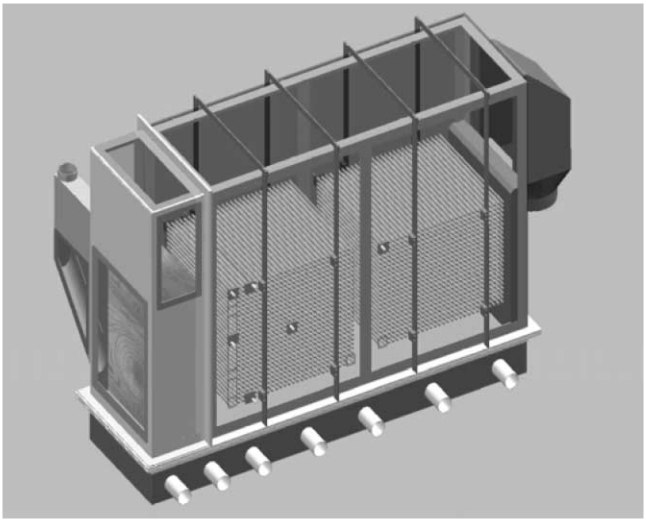

Figure 5: Fluidized bed heat exchanger, 3D view.

Supercritical Chemical Looping Combustion CFB Boiler

Increasing the steam cycle efficiency is a key option to significantly contribute to the reduction of CO_2 to be stored. In this particular case of CLC of refinery fuel gas, elevated feedwater, superheater, and reheater outlet temperatures are achievable. The noncorrosive air depleted stream in a CLC boiler is well suited to these super critical steam conditions, possible only above 350 MWe with 3 and 4 cyclones configurations.

Further stages of development include investigations of appropriate waterwall designs for circulation, taking advantage of the low heat flux in the air reactor and then not requiring riffled tubes, the analysis of system requirements for dynamic behavior, and approaches to further increase cost effectiveness of the supercritical CFB design (Figure 6).

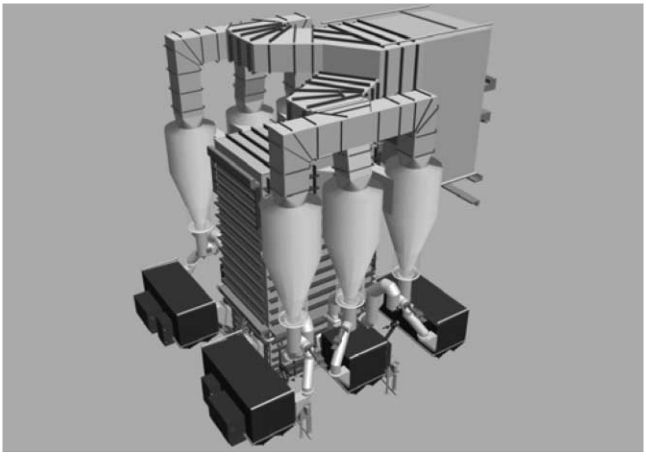

Figure 6: 600 MWe CFB boiler, 3D view.

CONCLUSIONS

ALSTOM Power Boilers has developed a design concept for large-scale CLC boiler firing refinery gas using existing CFB technology with fluid bed heat exchangers.

It appears that there are no hard points in terms of technology which reuses mostly existing CFB technology. The oxygen carrier is the main issue in terms of cost and durability.

CLC technology for refinery and natural gas combustion using CFB boilers might appear as a leading technology in terms of competitiveness for CO_2 removal and quick access to the market after a long-term prototype operation and a demonstration unit operation. CLC of refinery fuel gas using CFB technology has the potential to become an attractive option for integrated CO_2 capture power plants firing refinery and natural gas. The longer term development of the supercritical steam cycle adaptation to CLC of refinery fuel gas using CFB technology appears as a real possibility and a limited challenge.

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