Oxy-combustion CPU – From Pilots Towards Industrial-scale Demonstration

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Oxy-combustion CPU – From pilots towards industrial-scale demonstration

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Abstract

The CPU (Compression and Purification Unit) is used to capture, purify and compress the CO_2 contained in oxy-combustion boiler flue gas. Therefore, it plays a key role in the oxy-combustion route for carbon capture and storage (CCS). Over the last ten years Air Liquide has been developing this technology from a conceptual stage towards industrial maturity.

Since the last GHGT conference in 2012 [1], significant progress has been made. The objective of this paper is to present an overview of the progress made in developing the technology with a particular focus on results from pilot plants, and the intended application of key technology developments to the FutureGen 2.0 project.

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Keywords: CO_2, CCS, CPU, Oxy-combustion, Pilots

1. Introduction

To be ready for commercialisation, CCUS using oxy-combustion technology must first be proven at pilot-scale and then at industrial-scale. One of the technologies that must be tested is the CPU (Compression and Purification Unit) for purifying and compressing the flue gas. The Figure below shows the main steps in the development roadmap for Air Liquide's CPU technology (marketed under the name Cryocap™ Oxy).

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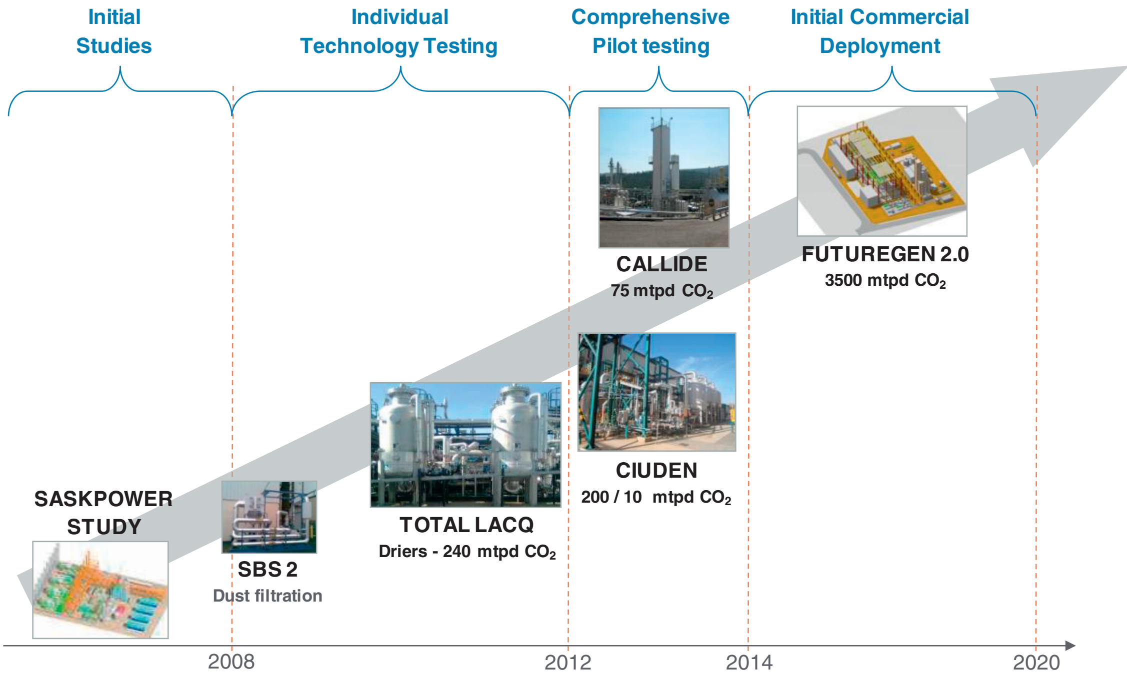

Fig 1. Air Liquide's roadmap for CPU technology development

Initial conceptual studies enabled the first process schemes to be developed and key technologies requiring pilot-scale testing and development to be identified. The next stage was to start pilot tests. This began with pilots testing one particular technology and culminated with the plants at CIUDEN and Callide where complete CPUs were operated. The final step is to start commercial deployment. This is currently planned to take place through the FutureGen 2.0 project.

The following sections will discuss the key parts of the technology roadmap focusing on the pilot plants and the most recent technology developments.

2. Lacq CPU dryers

The Lacq project is the first complete pilot of oxy-combustion with carbon capture, transport and storage. CO_2 is captured from a 30 MWth natural gas oxy-combustion boiler at TOTAL's Lacq site. Air Liquide provided the ASU, proprietary oxy-burner technology and a flue gas drying unit. Once the CO_2 has been dried and compressed it is transported by pipe to injection in a depleted gas field.

The dryers are specifically designed for the oxy-combustion application and the acidic nature of the gas to be treated. Therefore, the tests being carried out on the dryer units have been of particular importance for the development of the CPU design. Furthermore, the FutureGen 2.0 CPU uses a similar same design for the dryers, up-scaled accordingly.

The pilot was run for more than 12 000 of hours between 2010 and 2013 with various regeneration gases and NO_X content in the feed gas. The results allowed good progress to be made in understanding the following topics:

- Adsorbent qualification (ageing, performance): <1ppm H_2O at the exit was achieved

- Mapping of NO_X and nitric acid throughout cycle: NO_X pass through was estimated
- Vessel materials qualification CPU Pilot at Callide: Materials that could resist the highly acidic condensates and high temperatures (>100°C) were proven

3. CPU pilot at Callide

3.1. Overview

Specific details of the Callide Oxyfuel Project have been published by Spero et al (2014) [2]. The Callide CO_2 Purification Unit (CPU) is an experimental plant designed and built to test oxy-combustion on a coal furnace at semi-industrial scale. Flue gas entering the CPU comes from a small utility boiler where oxy-combustion process and equipments are being tested. This experimental boiler is a retrofitted 30MWe industrial installation from a former air-based operational plant. The CPU is designed for a capture of 75 tons of CO_2 per day.

Fig 2. Callide CPU pilot plant

The pilot plant is equipped with a wide variety of sensors, especially for gas and liquid analyses. Many species can be analysed throughout the process: CO_2, O_2, N_2, Ar, H_2O, NO, NO_2, CO, HCl and Hg. Form process condensates, ions such as SO_4^{2-}, SO_3^{-}, NO^{3-}, NO^{2-} are also analysed.

The CPU has been operated since the end of 2012. R&D test campaigns were performed, as well as maintenance and inspections. 4600 hours of operating hours have been cumulated for the warm part and 2800 hours for the cold part. Some 6800 tonnes of CO_2 have been captured from late 2012 to June 2014 during 2800 hours. The CO_2 recovery rate as measured across the cold box has reached 85%.

3.2. Inlet gas from oxy-combustion boiler

Flue gas composition varies with boiler operating mode. Typical flue gas composition is given in the table 1. It corresponds to a boiler power output of 28MWe.

Table 1. Inlet flue gas composition at CALLIDE CPU pilot

Process Data	Molar Composition (standard deviation)
O_2 %dry	4.8 (±0.6%)
CO_2 %dry	66.1 (±0.5%)
CO ppmv	332 (±63%)
SO_2 ppmv	1037 (±6%)
NO ppmv	666 (±12%)
NO_2 %dry	0 (±0.7%)
H_2O %	25.3 (±0.2%)

3.3. Quench & Low Pressure Scrubber

The first part of the process utilises a caustic soda (NaOH) wash through a Quench column and low pressure scrubbing column in series to effectively remove acid gases such as HCl and HF from the flue gas stream to levels below 10 ppmv. This reduces corrosion risk in the downstream CPU process. The scrubbing columns utilise a water spray system with a make-up and blow-down systems and injection of caustic soda at 50% (w/w) and process control to around pH 6.5.

The scrubbing columns are also effective in reducing the concentration of particulates (typically within the 10 to 100 µm size range) in the CPU feed stream from a nominal 30 - 50 mg/Nm^3 to less than 1 mg/Nm^3.

3.4. Filtration devices

The flue gas low pressure scrubbing is followed by a two-step dry dust filtration. The first step uses regenerative cartridges and the second a static non-regenerative filter. These filtration steps remove particles greater than 1 or 2 µm size. The filtration device easily reaches the objective: overall dust quantity under the 10µg/Nm^3 threshold, ensuring a safe operability of the downstream compressor.

The regeneration pattern of the dynamic filter was not observed due to the extremely small quantity of dust reaching the dynamic filter after the quench & scrubber skid.

3.5. Compression system

The flue gas is then compressed using a four-stage integrally-geared centrifugal machine. This technology is representative of that which would be used on large-scale plants.

Under the increased pressure conditions, and in the presence of free O_2 and water, the NO is converted to NO_2 and HNO_3 which are extracted from the process gas as condensates via the coolers. These condensates typically exhibit pH < 1. No significant corrosion has been observed in the compressor or cooler parts.

3.6. Driers

Before entering the cold box where the gas is cooled down and condensed at very low temperature (~-50°C), it is dried to under 1ppm water content. A horizontal bed of adsorbent is used in this purpose. The dryers exhibit a very satisfying behavior with dew points less than -95°C.

In this part of the process, during the dryers production phase, NO_2 is adsorbed. When H_2O and NO_2 are co adsorbed, HNO_3 is formed and adsorbed. As a result, nitric oxide is found in the condensates and in the gas during regeneration. In the condensates, pH can reach -1 due to nitric acid dissociation.

3.7. Cold Box – De-NO_X column

In order to remove the remaining NOx species contained in the gas, a rectifying column is used. Pure liquid CO_2 enters at top column inlet and scrubs the inlet gas on a structured packing.

3.8. Cold Box – Incondensable gases

A first separation of 'light' and 'heavy' gases is made when the flow reaches -50°C. Incondensable gases are purged and used for driers regeneration. This stream contains around 32% of CO_2 and represents a loss of CO_2 of 12%-15% of total inlet CO_2 moles. This recovery was lower than the 90% target due to lower than expected CO_2 concentration in the flue gas resulting in lower CO_2 partial pressure in the cold box.

3.9. Cold Box – De-Ox column

The De-Ox column aims at removing the remaining 1.5% of light components (N_2, O_2, Ar) in the impure CO_2. The column allows purification of the CO_2 down to 10ppm of oxygen. The composition of the produced gaseous CO_2 is given in table 2.

Table 2. CO_2 product purity from Callide A CPU pilot

Compound	Concentration
CO_2	>99.95%vol
O_2	<10ppm
SO_2	<0.1ppmv
NO	<2.5ppmv
NO_2	<2.5ppmv
H_2O	<1ppmv

In addition to producing CO_2 of very high purity, the cold box demonstrated the auto-refrigeration principal since it is cooled by evaporation of the liquid CO_2 product.

Furthermore, in order to demonstrate the most energy efficient process possible, it was important to demonstrate that the cold box could be operated close to the triple point. This is because operation at cold temperatures gives the highest energy efficiency. This was successfully achieved without freezing of CO_2 causing operational issues via plugging.

4. CPU pilot at CIUDEN

4.1. Overview

CIUDEN, in Northwest Spain, is a large pilot platform for CCS technologies. Its facilities include both an oxy Circulating Fluidised bed CFB (30MWth) and Pulverised Coal (PC) (20MWth) boiler with flue gas cleaning systems.

The CPU pilot plant at CIUDEN was supplied by ISOLUX using Air Liquide design and technology and commissioned in 2012. The warm part (SO_X scrubbing, filter and dryers) has a capacity of around 160 tpd CO_2. The cold box has a capacity of 10 tpd and purifies the CO_2 by distillation. To date, the warm part has operated for around 2500 hrs and the cold part for 1500 hrs.

Fig. 3. CPU Pilot Plant at CIUDEN.

4.2. Scrubber

The first step in the process is a quench followed by a scrub with Na_2CO_3 solution in order to remove the most acidic gases such as SO_2, HCl and HF. This reduces corrosion risk in the downstream CPU process. The scrubbing takes place in two plastic towers placed in series.

The quench and scrubber were made from hastelloy and plastic respectively and neither showed any signs of degradation. This was also the case for the coating used on the flue gas inlet.

The scrubber achieved the required SO_2 concentration of <1ppm. Some spikes above this value were observed when the levels of SO_2 in the flue gas rose. However, their duration was typical no longer than a few minutes. Waste pH was measured in the range 6-7 for a reagent pH of 11-9.

4.3. The high performance filtration system

The next step in the process is a high performance filtration system. As on the Callide plant it consists of two steps, the first using regenerative pleated polymer-based cartridges and the second a static non regenerative filter.

During the operation of the pilot, negligible dust removal by the filtration system was observed. It would appear that almost all the dust remaining in the flue gas is removed in the scrubber since dust build up was observed in the bottom of the towers. These results would suggest that the filtration step is not necessary. However, feedback from the Callide pilot discussed above would suggest that scrubber dust removal may not always suffice.

4.4. Low Pressure drying system

CPU designs have generally used a drying step downstream of the flue gas compression. A key objective of the CIUDEN CPU pilot was to test an alternative system where the flue gas is dried before the main flue gas compression. The flue gas contains more water at lower pressure so more adsorbent is required. However, the flue gas is then ‘bone dry’ and there is no longer any risk of nitric or sulphuric acid formation downstream. This means that carbon steel may be used in the flue gas compressor instead of more expensive alloys.

The drying system has given very positive results with a water dew point of -100°C at the outlet being attained. This is more than sufficient for the cold box where minimum temperatures are around -50°C.

4.5. Compression

Following the dryers, round 15% of the flue gas is compressed to ~20bara in order to feed the cold box. By reducing the flow of gas to the compressor plant investment was optimised. Due to the small volume flow reciprocating technology was used. Since large-scale plants will use integrally geared centrifugal compressors, this part of the pilot did not aim to demonstrate up-scalable technology. This was performed on the Callide pilot discussed above.

4.6. Cold Box

The flue gas undergoes cryogenic processing in a cold box. The CO_2 is removed from the bulk of the flue gas via partial condensation at ~-50°C. The refrigeration required in order to reach this temperature is provided by a closed-loop CO_2 cycle. Auto-refrigeration cannot be used since a CO_2 product in liquid state was required.

In order to reach 99.9% purity, distillation is required in particular to remove NO_X and O_2. As discussed above, in order to improve the efficiency of the process it is important to perform the partial condensation step at a temperature as close to the triple point as possible.

Results concerning CO_2 purity were very encouraging. Typical values for measured purity are given in the table below:

Table 3. CO_2 product purity from CIUDEN CPU pilot

Compound	Concentration
CO_2	99.9%vol
SO_2	<0.1ppmv
NO_X	<10ppmv
H_2O	<1ppmv

Furthermore, as on the Callide plant over the whole operating period, no issues with internal cold box plugging due to CO_2 freezing were encountered.

5. Air Liquide's near-zero emissions CPU

Due to recent improvements to its process solutions based on pilot plant tests results and on-going technology development, Air Liquide has designed a CPU that reduces atmospheric emissions to approximately zero and captures up to 98% of the CO_2 emitted by the boiler.

The increased CO_2 recovery enables significant savings on specific CO_2 capture costs. The avoidance of air emissions of pollutants such as CO and NO_X, means that nitrogen, oxygen and argon are almost the only gases emitted.

5.1. Increasing CO_2 recovery to decrease GHG emissions and to reduce specific cost of capture

To decrease the CO_2 emissions to very low levels while keeping capture costs reasonable, Air Liquide has coupled cryogenic purification with specially developed ultra-CO_2 selective membrane technology on the non-condensable gases. This membrane technology enables drastic reduction of oxygen and nitrogen permeation.

The process increases CO_2 recovery since CO_2 permeates through the membranes and is then recycled to the main flue gas compression chain of the CPU in order to be condensed in the cold box. Therefore, reducing oxygen permeation involves a reduction of the flow rate of this recycle stream and consequently enables power and capital costs savings.

Due to this innovative process arrangement, a CO_2 capture rate of 98% appears achievable in steady-state operating conditions with flue gas having a sufficient CO_2 concentration (>~84%vol dry basis). Allowing for full start-ups, shut-downs, and transients, this should enable demonstration of 90%+ capture on an annual average basis for a full plant. This improvement comes without any modifications to either the Air Separation Unit (ASU), the boiler or the 'standard' flue gas cleaning systems upstream of the CPU (FGD, baghouse etc…). It is estimated that this increase in capture rate could reduce the specific levelised cost of CO_2 capture by around 5-10%.

5.2. Reducing CO and NO_X emissions

In parallel, Air Liquide has also made significant efforts to reduce the emissions of other pollutants to the atmosphere.

Firstly, in order to reduce CO emissions, a catalytic oxidation reactor using oxygen already contained in the flue gas has been implemented. With this system, the CPU is able to stop 98% of the CO produced by the boiler. This equipment would have a significant cost impact on post-combustion processes due to the dilution of carbon monoxide in the nitrogen that comes from the combustion air. In the oxycombustion configuration, the size of this reactor is also reduced because of the low mass flow and high pressure of the treated vent gas of the CPU. It is an interesting advantage of oxycombustion processes compared to post-combustion ones.

Following recent tests on its pilot plants, Air Liquide has obtained interesting results concerning the behavior of NO_x in the wet flue gas compressor and also in the dryer. In particular, significant removal was observed in the compression and drying steps. Therefore, the CPU process was modified to use membranes to selectively recycle NO_X and CO_2 from the off-gas of the cryogenic purification via the dryers (as regeneration gas) to the inlet of the compressor. In this way both the NO_X adsorbed in the dryers and those released from the cryogenic purification are sent back to the compressor where they are removed in the form of nitric acid in the condensates at each intercooler. This process results NO_X abatement of approximately 90% without new equipment and without efficiency loss. Furthermore, an SCR upstream is not required.

6. FutureGen 2.0 FEED – Towards industrial-scale demonstration

Building on the results from pilot plants, the FutureGen 2.0 Pre-FEED studies and internal development programmes, Air Liquide brought the technology to a point where a FEED study could be launched as part of the FutureGen 2.0 project.

6.1. FutureGen 2.0 Project – key facts and status

The FutureGen 2.0 project objective is to repower an existing plant in Meredosia Illinois with oxycombustion technology. The size is ~168MWe gross and the objective is to capture 1 million metric tones CO_2 per year. The design is now sufficiently mature to move straight into a project execution phase. The work that has been completed as part of the FEED includes the following:

- Utilities Flow diagram
- Plot plan
- Full PIDs and PFDs
- Electrical one line diagrams
- Instrumentation lists
- HAZOPs (including for interfaces)
- Process control strategy

The FEED commenced in April 2012 and is now completed and the next step is the go/no-go decision to move into project execution.

6.2. FutureGen 2.0 Project – process & technology description

The block flow diagram for the process is shown in the figure below.

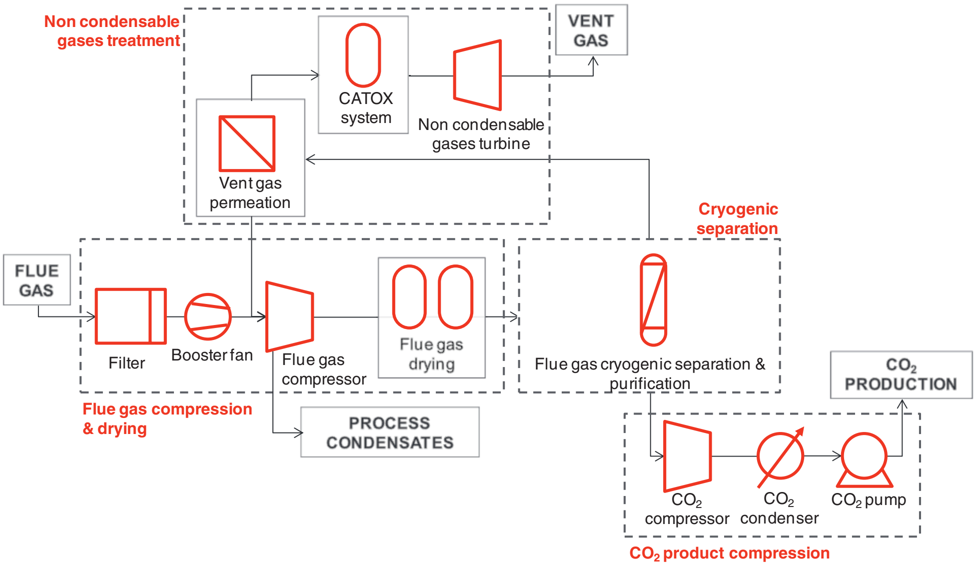

Fig 4. FutureGen CPU – block flow diagram

The flue gas exits from the boiler at roughly atmospheric pressure and following a scrub enters the CPU. The first step is a high performance filtration system using pleated cartridges similar to those tested at Callide and CIUDEN.

It is then compressed first in a booster fan and then to the pressure of the cryogenic process in a multistage, integrally geared, centrifugal compressor. A significant part of the NO_X is stopped and evacuated through the process condensates as nitric acid.

As discussed above, before entering the cryogenic process, the pressurized flue gas must be dried to avoid water freezing and to achieve pipeline specification in terms of water content. The chosen adsorption drying system is based on the design that has been successfully tested at the Lacq and Callide pilot plants. It consists of a Temperature Swing Adsorption (TSA) unit with an appropriate adsorbent. The flue gas is dried in one bottle while the other bottle is regenerated and prepared to return to drying. A significant part of the remaining NO_X is also stopped by the drying unit.

The dried flue gas enters the cryogenic part where it will be purified, separating non-condensable gases like N_2, Ar, O_2 from CO_2. The process is similar to that used on the Callide and CIUDEN pilot plants in that the CO_2 is separated from the flue gas via partial condensation at ~-50°C. As on the Callide pilot plant, the cold is provided by evaporating the liquid CO_2 produced. Purification of the CO_2 is achieved using distillation in a similar way to that tested at both Callide and CIUDEN.

The non-condensable gases exiting the cryogenic section are then processed through a membrane unit where most of the uncondensed CO_2 is recovered back into the CPU flue gas compression chain. The membrane technology is advanced hollow fibre and is owned and manufactured by Air Liquide through its membrane division, MEDAL.

After membrane permeation, the non-condensable gas is still under pressure and is subjected to catalytic oxidation where CO is oxidized to CO_2 with the oxygen already present in the gas. This reduces the CO emissions to a low level.

Lastly, the non-condensable gases are expanded with mechanical power recovery and vented to the atmosphere. One turbine train treating 100% of the non-condensable gases has been chosen. This is done in order to minimise cost and footprint.

The CO_2 product from the cryogenic section is further compressed up to a pressure sufficient to enable a significant increase of its density by cooling from ambient air. Dense CO_2 is finally pumped up to the pipeline pressure.

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