The CO₂ Capture Project

Status and Prospects of the Capture Program

Ivano Miracca*, Mark Crombieb, Jonathan Forsythb, Cliff Lowe,c
Gustavo Torres Moure,d, Mahesh Iyer,e, Mark Bohmf

aSaipem S.p.A. (Eni Group), Viale De Gasperi, 16, I-20097 San Donato Milanese, Italy
bBP Alternative Energy International Ltd., ICBT Chertsey Road, , TW16 7LN, Sunbury-on-Thames.UK
cChevron Energy technology Company, 100 Chevron Way, Richmond, CA, 94802-0627.U.S.A.
dPetrobras, CENPES, Cidade Universitaria Q.7, Ilha do Fundão, Rio de Janeiro, 21941-598, Brazil
eShell International Exploration & Production Inc., 200 N Dairy Ashford Road, Houston, TX, 77079, U.S.A.
fSuncor Energy Inc., 112 4th Avenue SW, T2P2V5, Calgary, Alberta, Canada

Abstract

The CCP is a partnership of several major energy companies supporting advancement of technologies toward deployment of industrial-scale CO₂ capture and storage. The paper describes the technology development projects in the field of CO₂ capture supported by the CCP during current phase III (CCP3, 2009-2013). Development work has focused on applications in three critical areas for the oil and gas industry: refining operations, steam production for heavy oil extraction, and natural gas-fired power generation.

Keywords: CO₂ capture, scale-up, power generation, oil refinery, oil extraction, postcombustion, precombustion, oxyfiring, chemical looping

1. Introduction

The CO₂ Capture Project (CCP) is an award-winning partnership of several major energy companies, working to advance the technologies that will underpin the deployment of industrial-scale CO₂ capture and storage. Since its formation in 2000, the CCP has undertaken more than 150 projects to increase understanding of the science, economics and engineering applications of CCS. The group has been working closely with government organizations – including the US Department of Energy, the European Commission and more than 60 academic bodies and global research institutes. The CCP is currently approaching the conclusion of its third phase, which is scheduled to run until the end of 2013.

The CCP Capture Team is focused on developing a suite of economically viable next generation technologies. Much of this work has focused on applications in three critical areas for the oil and gas industry: refining operations, steam production for heavy oil extraction, and natural gas-fired power generation. This has involved conducting research into reducing cost uncertainties and identifying the best options to take forward. This work has entered the critical phase of field demonstrations:

- An oxy-combustion trial has been carried out on a pilot-scale Fluid Catalytic Cracking (FCC) unit – one of the highest CO₂ emitting units in a refinery. The test is expected to bring closer a cost-effective technology capable of capturing up to 95% of FCC CO₂ emissions, potentially equating to some 20-30% of emissions from a typical refinery. Detailed results are presented in a dedicated paper.

*Corresponding author: Tel: +390252043450 e-mail: ivano.miracca@saipem.com
The retrofit for oxy-firing of a commercial Once Through Steam Generator (OTSG) used in oil sands extraction operations in Canada (duty of 50 million BTU/hr) is under way, following completion of a feasibility study by Praxair. A demonstration run is scheduled in the spring of 2013.

An assessment of the performance and economics of state-of-the-art post combustion, oxy-firing and pre-combustion for refining operations, steam production for heavy oil extraction and natural gas power generation has been carried out. Foster Wheeler was commissioned to conduct technical evaluation studies, while an in-house economic model was developed, which included capture, transportation, and storage costs. The objective of these studies was to provide material for a CO2 capture handbook to be used to support CO2 capture technology selection in the oil and gas industry. CCP3 is also supporting the development of capture technologies to the level of "ready for field demonstration" by the end of 2013 and the screening of novel technologies to identify potential breakthrough reductions in capture costs. All of the technologies under development in CCP3 timeframe will then be evaluated with the objective to identify "preferred" technologies for each scenario. This knowledge, coupled to the achieved technical progress, will set the path toward large-scale implementation.

For each area of application the paper describes the projects carried out and the main findings.

2. Capture technology for oil refineries

Refineries are responsible for some 6% of total emissions of CO2 from stationary sources worldwide (by contrast power stations account for more than 80%), amounting to 0.8 billion tons per year. The level of specific emissions from a single refinery depends on the process configuration, mix of crude inputs, and types of products produced, but is broadly in the same range as the level of specific emissions from a large power station. For example, a world-scale refinery processing 250,000 barrels per day of crude oil may emit between 4 and 5 million t/y of CO2, versus 3.5 million t/y generated by a 500-MW coal-fired power station. The carbon footprint of refineries could increase further as increasingly heavy oils are used as feedstock. In theory pre-combustion and oxy-firing CO2 capture technologies are better candidates than post-combustion for a refinery. While post-combustion would need at least one capture unit per stack, both pre-combustion and oxy-firing, ideally could allow centralised capture, minimising concerns regarding plot space availability that are typical in a space-constrained refinery application.

A typical refinery has a wide range of CO2 emission sources, including fired heaters, boilers and process units, with multiple stacks emitting flue gas to the atmosphere. In this multi-source environment, two major emitters may be identified depending on the specific process scheme:

- The regenerator of the FCC unit
- The hydrogen production unit (usually a steam reformer)

The combination of these two processes may account for up to 50% of CO2 emitted at a given refinery. Therefore, they are the primary targets for reducing refinery greenhouse gas (GHG) emissions. Another large share of emissions (≈ 40% of the total) is represented by boilers and fired heaters (even more than 50 units, usually grouped in clusters and discharging to several stacks).

Projects related to capture from FCC units, as well as from heaters and boilers have been carried out in CCP3.

2.1. Capture in the FCC unit

The FCC process catalytically converts heavy oil fractions to lighter products such as Liquefied Petroleum Gas (LPG) and gasoline. During the reaction step, coke is formed as a by-product and deposits on the surface of the catalyst, which is then deactivated. The coke needs to be burned off in the regenerator to restore catalyst activity. Oxy-combustion is the only alternative to post-combustion for CO2 capture from the FCC, and in the oxy-combustion process the air normally used for combustion of the coke is replaced by pure oxygen, which is diluted with recycled CO2, to maintain the thermal balance and for catalyst fluidisation in the FCC.

The CCP has previously conducted a techno-economic evaluation of oxyfiring and post-combustion amine absorption for CO2 capture from the FCC regenerator. Both processes were able to achieve the required specifications and recovery level. Although the post-combustion option had a lower capital cost, the lower operational costs for oxyfiring delivered a lower overall capture cost. Evaluations performed in CCP3 confirm that oxy-firing is economically competitive with post-combustion for this application.

The CCP and Petrobras set up an oxyfiring field demonstration at Petrobras’ SIX testing facility in Parana state, Brazil, testing different operational conditions and feedstocks to demonstrate that stable operation may be maintained operating the regenerator in oxy-combustion mode and to obtain reliable data for scale-up.
The pilot FCC unit (Figure 1) has the capacity to process up to 33 b/d of hydrocarbon feed (emitting 1 t/d of CO₂). It consists of an adiabatic riser, stripper and regenerator, which allows simulation of a commercial FCC unit, including the energy balance. The retrofit of the unit involved the design, construction and installation of an oxygen supply system (OSS) and a CO₂ recycle system (CRS). Oxygen is stored in a liquid state and vaporised before injection in the regenerator. The CRS is skid mounted and includes catalyst fines removal, sulphur oxide (SOₓ) removal, recycle compressor and a CO₂ temporary storage vessel.

The test program, performed in 2011-2012 demonstrated steady operation in oxy-firing mode, achieving CO₂ concentration up to 95% vol. in the flue gas. CO₂ has a much higher specific heat than nitrogen. As a consequence more sensible heat may be absorbed by the gas in the regenerator, so that the FCC unit may operate at a higher throughput (≈ 10%) or process heavier (lower cost) feeds [1]. This results in further advantage for the oxy-fired option when performing a complete economic evaluation.

The need for particular care in the design of the flue gas recycle system to avoid corrosion in the recycle compressor is another important lesson learnt during the testing. While the root causes for corrosion experienced during the tests have been fully understood, an overall optimization of the recycle/purification/compression system would be advisable before proceeding to scale-up.

2.2. Boilers and Fired Heaters

The technical feasibility of oxy-firing for natural gas fired boilers was already demonstrated by Total in their Lacq demonstration [2]. Previous simulations in CCP however showed that fired heaters may pose more problems in replicating the heat flux profile when shifting from air to oxy-combustion. While specific burners for oxy-combustion are under development by several vendors, in the case of retrofit the use of existing burner systems with some modifications, if needed, would be preferable. Costs for retrofit would be decreased and chance of shifting between combustion modes would be guaranteed.

The CCP therefore commissioned the John Zink Company to conduct oxy-fired testing on two of their conventional process heater burners, an SFG staged gas low NOₓ burner and a COOLstar® Ultra-Low NOₓ burner. The heart of the project, single burner testing for both burners, took place at John Zink’s state-of-the-art test facilities in Tulsa, Oklahoma (Figure 2). Both burners were tested with natural gas and simulated Refinery Fuel Gas (RFG). The project was concluded in June 2012. Both burners performed satisfactorily under oxy-firing conditions with no performance issues. Transition between air and oxygen was successfully performed several times. The level of air in-leakage was
higher than expected. Achieving less than 10% vol. nitrogen in the flue gas is likely to be a major challenge, adversely affecting downstream CO₂ purification costs. Oxy-firing remains a more viable option for systems with boilers, operating at a positive pressure in the firebox. Mode details about this project may be found in [3].

Pre-combustion is an interesting option for the refinery. In contrast to post-combustion and oxy-firing, no plot space would be needed close to the existing refinery units. Refineries are already producing hydrogen for use in hydro-treatment processes. In the prospect of CO₂ capture most of the fuel used could be decarbonized, by conversion to hydrogen in a large production unit. According to CCP economic evaluations, this option, using state-of-the-art Autothermal Reforming Technology (ATR) would be competitive with post-combustion in terms of CO₂ avoidance cost. Previous work by Chevron [4] showed that current burners may work in hydrogen firing mode.

During the past phases the CCP supported development of several capture technologies for application to pre-combustion schemes with the objective of making further reductions in the cost of capture for several applications (including power generation from natural gas in combined cycle [5]). CCP3 has decided to investigate one of these technologies, Membrane Water Gas Shift (MWGS), in more detail, to assess the potential of improvement compared to state-of-the-art. While in state-of-the-art technology CO₂ would be captured downstream of the Water Gas Shift (WGS) unit by solvent absorption, in MWGS hydrogen permeable membranes would be used to bring the shift reaction to completion (achieving a stream ideally composed by hydrogen and CO₂ only) while separating the hydrogen through membrane permeation and leaving a stream highly concentrated in CO₂ at relatively high pressure (20-30 bars).

The CCP therefore commissioned the Pall Company to perform intensive testing of their palladium alloy membranes, first in the form of 12 inch long tubes and later in modules composed by 12 tubes that may become the base for scale-up to a field pilot. Tests will supply the parameters for sizing and costing modules for a commercial unit to verify whether application of this technology may reduce costs compared to state-of-the-art. The project is scheduled for completion by September 2013.

3. Capture technology for extraction of heavy oil

The in-situ extraction of oil sands or bitumen requires large amounts of steam, using the Steam Assisted Gravity Drainage (SAGD) technique. A pair of horizontal wells are drilled into the reservoir, one a few meters above the other. Steam is continuously injected into the upper wellbore to heat the oil and reduce its viscosity, causing the heated oil to drain into the lower wellbore, where it is pumped out.

Once-through steam generators (OTSG) are the primary technology used in oil sands operation for producing this steam. These boilers use significant amounts of natural and/or produced gas, and are expected to be a major source of growth of GHG emissions in countries such as Canada since upwards of 85% of the country's oil sands are suited to in-situ methods of extraction. This is an important area of development which could significantly reduce the greenhouse gas emissions of these operations, both for new build and existing operations.

In 2013 the CCP joined by Cenovus Energy, Devon Canada, MEG Energy, Praxair, and Statoil is demonstrating oxy-fuel combustion technology to reduce CO₂ emissions from OTSG. The projects started with a feasibility study to assess the cost of retrofit for a typical commercial cluster of OTSG (4 boilers, 250 million BTU/hr each) and for the boiler designated for the demonstration (50 million BTU/hr boiler operated by Cenovus in the Christina Lake extraction site (figure 3)). The project has now entered the demonstration phase, partly funded by the Government of Alberta through the Climate Change and Emission Management Corporation. Between May and June 2013 demonstration will take place using the original burner with modifications.

Chemical-looping combustion (CLC) is a combustion technology where an oxygen carrier is used to transfer oxygen from the combustion air to the fuel, thus avoiding direct contact between air and fuel. The technique involves the use of metal oxide particles with the purpose of transferring oxygen from an air reactor to a fuel reactor. In the fuel reactor, the fuel in gaseous form reacts with the metal oxide generating CO₂ and H₂O, and in the air reactor the reduced metal oxide is re-oxidized by oxygen contained in the air.

During the previous phases the CCP supported formation of a Partnership, including Chalmers University of Technology, Consejo Superior de Investigaciones Cientificas (CSIC), Technical University of Vienna (TUV) and Alstom Boilers. This Partnership, in the frame of R&D projects co-funded by the European Community, brought the technology from the almost pure conceptual level (2000) to development of a very active Ni-based oxygen carrier and operation of a 10 kW unit with continuous solid circulation hosted by Chalmers (2003) and finally to operation of a 120 kW unit hosted by TUV (Figure 4) (2007). Evaluations in CCP2 confirmed that this technology might represent a breakthrough with a considerable reduction in capture costs.

A CLC boiler system, being made by two vessels, has a larger plot plan than conventional boilers. This is a strong constraint for application to refineries, in which CO₂ capture will mostly be a matter of retrofitting existing equipment. In contrast the extraction of heavy oil is an expanding area where new-built plant will play a major role and plot plan
constraints are milder. CLC could therefore become the ideal solution for next generation capture technology in this field.

CCP3 is supporting work by CSIC and Vlaamse Instelling voor Technologisch Onderzoek (VITO) to prepare and test copper based carriers as a cheaper alternative to nickel-based carriers previously developed. In the same frame TUV and the boiler manufacturer Bertsch are collaborating to fill the remaining gaps in detailed design of larger scale CLC boilers to deliver sizing and costing for a 10 MW demonstration boiler as well as for the typical cluster size currently used in SAGD operation. This project is scheduled for conclusion in September 2013.

The scale of operation in Canadian extraction is too small to make pre-combustion competitive. Future expansion might however lead to larger clusters of boilers in a relatively small area, making pre-combustion more appealing for this application.

---

4. Capture technology for Natural Gas Combined Cycle (NGCC) power stations

This is a difficult application, since the low concentration of CO₂ in the flue gas (4% vol.) apparently penalizes post-combustion resulting in larger equipment and possibly higher energy consumption than for coal-based power generation. CCP2 carried out a thorough investigation of state-of-the-art and future pre-combustion technology in search of cheaper alternatives to post-combustion with several technology providers in the frame of the EU-funded project CACHET. The conclusion was that, either today or in the next decade, pre-combustion cannot challenge post-combustion due to lower efficiency and high capital cost [6]. Evaluations in CCP3 confirmed that commercial state-of-the-art post-combustion technology already tested at a relatively large scale (though still one order of magnitude smaller than needed for a 400 MW power station) would cause a drop in efficiency of only ∼ 12% (from 57% to about 50%). The CCP3 consequently engaged in a screening process of novel post-combustion technologies through studies, lab and pilot testing. As part of this process the CCP joined the PCO2C Partnership, a multiphase program, co-funded by the US Department of Energy, run by the Energy and Environment Research Center (EERC) of the University of North Dakota. One of the main tasks is pilot scale (Figure 5) testing of novel post-combustion technologies including novel solvents characterized by low energy consumption and/or enhanced kinetics, multiphase systems, solid sorbents, high efficiency packings and novel contactors applying process intensification principles. The current phase of PCO2C will be concluded by December 2012. The results, coupled to results obtained by the CCP independently in other projects for evaluation of specific technologies, will form the base to assess the potential for future cost reduction of post-combustion capture for NGCC.

An extended test program has already been agreed with EERC taking place during the first quarter of 2013. The pilot plant will be modified to be tailored to the needs of a technology proposed by Ion Engineering. Ion is developing a proprietary system in which an amine solvent is used in solution with a high-boiling temperature ionic liquid rather than in aqueous solution. In this way water evaporation in the desorption phase is avoided, considerably reducing the energy consumption of the capture system. Other specific test programs may be planned during next year.

Recycle of part of the flue gas to the combustion chamber (EGR – Exhaust Gas Recycle) was studied in the past by the CCP in collaboration with General Electric. This would increase the concentration of CO₂ in the flue gas to levels similar to coal-fired systems, with possible reduction in capital cost and energy consumption. The experimental project demonstrated that up to 35% flue gas may be recycled to the combustion chamber without affecting the performance of
a 9-F type turbine. This activity was not continued in CCP3 because the overall energy consumption of state-of-the-art solvents does not seem to be much affected by CO₂ concentration in the flue gas. Novel technologies might however receive more benefit by the use of EGR and alternative recycle schemes have been proposed, minimizing the percentage of flue gas to be recycled to achieve a given concentration of CO₂. The CCP might therefore reconsider EGR in the final part of CCP3 as an option to reduce capture costs for NGCC power stations.

Finally, oxy-firing was considered in the past, because several authors proposed novel high efficiency cycles based on oxy-combustion [7]. This activity was however terminated after initial evaluations because the development of novel types of turbine would be needed to realize the benefits of these cycles. Activity might be re-considered in case turbine vendors get involved in this type of development.

Fig. 5. The pilot test unit for novel solvents at EERC (Courtesy of EERC)

Acknowledgements

The Authors, on behalf of the CCP, acknowledge contribution by the U.S. Department of Energy and the Climate Change and Emission Management Corporation of the Government of Alberta. They also wish to thank all technology providers involved in CCP projects for their continuing engagement and fruitful efforts.

The CO₂ Capture Project (CCP) is an award-winning partnership of several major energy companies, working to advance the technologies that will underpin the deployment of industrial-scale CO₂ capture and storage. Current Phase Three (CCP3) members are: BP, Chevron, Eni, Petrobras, Shell and Suncor.

References


