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OXYFUEL TECHNOLOGIES FOR CO_2 CAPTURE: A TECHNO-ECONOMIC OVERVIEW

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ABSTRACT

The CO_2 Capture Project (CCP), a joint partnership of eight major energy companies, continues to seek solutions to the challenges presented by climate change issues. The CO_2 Capture Project, working with a wide selection of technology providers from both industry and academia, has continued to develop a range of technologies to reduce the cost of capturing and storing CO_2, across three broad categories; post-combustion, oxyfuel and pre-combustion decarbonisation.

Over the last three years, a series of studies focusing on oxyfuel combustion (i.e. using pure oxygen rather than combustion air as the oxidant) have been undertaken. These studies have assessed the potential application of oxyfuel technologies to both heat and power production systems. This paper provides an overview of these studies, which range from in-depth engineering feasibility assessments to high level reviews of developmental technologies.

The technologies considered by the CCP include, amongst others, the oxyfuel firing of heaters and utility boilers (using both cryogenic distillation and ion transport membrane separation of oxygen); advanced zero emission power cycles (using oxygen transport membranes) and chemical looping combustion for oxygen separation in advanced boiler systems.

The technologies will be reviewed and their range of potential application assessed from a technical perspective. Where available, comparative process economic costs for the differing technologies will also be presented, allowing conclusions to be drawn regarding the relative attractiveness of the different options as a means of providing high purity CO_2 for transportation and subsequent storage.

INTRODUCTION

The concept of oxyfuel combustion (i.e. combustion of fuel using high purity oxygen rather than air as the oxidant) is not a new concept and is already routinely employed where high furnace temperatures are required, such as in the metallurgical and glass making industries. As an enabling technology for the capture and subsequent storage of CO_2, oxyfuel combustion is potentially attractive, as the product of combustion is a flue gas stream consisting largely of CO_2 and water, from which CO_2 is easily separated. However, without modifications to the combustion equipment, it is not suitable for retrofit to conventional heaters, boilers, process furnaces or gas turbines because of the very high combustion temperatures encountered during combustion.

In the longer term, development of more advanced materials may enable the direct application of oxyfuel combustion to those equipment types listed above but in the near term, attention has largely turned to the use of various diluents to moderate the combustion temperatures. Depending on the diluents selected and the degree of temperature moderation required, it is possible to retrofit existing combustion equipment for oxyfuel firing.

Previous studies have concluded that one of the most significant costs in any oxyfuel combustion scheme is the production of high purity oxygen. Cryogenic oxygen production is a mature technology and it is therefore anticipated that further optimisation of this technology may yield only incremental reductions in cost. A significant research and development effort is ongoing, outside the frame of the CCP, to develop novel oxygen separation technologies which can materially reduce the cost of air separation. Whilst this development is not driven by a

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requirement to capture CO_2, the application of these novel technologies may result in significant cost reductions in the field of CO_2 capture and storage.

Oxyfuel evaluations within the CCP

Over the last three years, the CCP has undertaken a wide selection of studies, considering technology developments for CO_2 capture under the three broad categories of 'Pre-combustion decarbonisation (PCDC)', 'Post combustion' and 'Oxyfuel'. Within the scenario based approach for assessing the technical applicability and economic attractiveness of capture technologies adopted by the CCP, oxyfuel technologies have been assessed in applications based upon new build or retrofit process heaters and furnaces; new build boilers; and gas turbines. Across these possible applications, the oxyfuel team have investigated:

- The application of cryogenic air separation technology with flue gas recycle to moderate combustion temperatures applied to process heaters and boilers in the European refinery scenario to establish a 'baseline' process design and cost;
- The application of novel heater and boiler designs which take advantage of oxyfuel firing to increase efficiency, reduce equipment size and potentially reduce costs compared to conventional fired equipment;
- Advanced thermodynamic cycles for power generation systems;
- Novel air separation technologies for application to conventional process heaters and boilers;
- Novel technologies integrating steam or power generation with novel oxygen purification techniques.

The Oxyfuel Baseline Study

A detailed feasibility study[1], led by Air Products in collaboration with Mitsui Babcock and Foster Wheeler, assessed the viability of retrofitting flue gas recycle based oxyfuel technology to a number of heaters and boilers in the European refinery scenario. Given that the process heaters and boilers are widely distributed across the site, a system of centralised cryogenic air separation to supply high purity oxygen to each unit was selected, with localised CO_2 drying and compression prior to collection and subsequent purification at a centralised location.

The overall scheme requires two world-scale cryogenic air separation plants (each providing 3,700 tonnes per day of 95 vol% O_2), capturing 2 million tonnes per year of CO_2 from a total of thirteen process heaters and seven utility boilers. Five distributed CO_2 drying and compression stations collect and send low pressure CO_2 to a centralised area for final CO_2 purification and export compression. The overall capture cost ($/tonne of CO_2 'avoided') for the basic scheme estimated by Air Products was found to be $43/tonne, which compared favourably with a benchmarked cost, generated by the CCP cost estimation team, of $50/tonne. These costs included purification of the CO_2, as discussed in the next paragraph.

A key consideration with retrofitting oxyfuel combustion onto existing combustion systems is the optimisation of oxygen and product CO_2 purity. Whilst provisions can be made to improve the sealing of combustion equipment against the ingress of 'tramp' air, some air ingress is unavoidable. Once inerts (N_2 and Ar) are present due to tramp air ingress, final product CO_2 separation is also required to reject these impurities from the product stream. This allows a lower purity (<99%) oxygen to be selected, since inerts in the oxygen will also be removed during final product treatment. Early optimisation of the baseline study indicated that using 95% oxygen in combustion provided an acceptable balance between the reduced cost of an ASU to generate lower purity oxygen and the requirement to provide equipment to separate inerts from the product CO_2 stream, targeted to reach 96.5% CO_2.

Overall, the baseline study showed that oxyfuel technology, as applied to a European Refinery scenario, is considered to be technically feasible at a low technical risk (although a commercial demonstration of the flue gas recycle technology is still required). Furthermore, cost savings of >30% are thought to be achievable when compared to the Post Combustion baseline[2], using amine scrubbing of flue gas streams to capture CO_2 at a cost of around $75/tonne.

Ion/Oxygen Transport Membranes for Air Separation

The oxyfuel baseline study also identified the significant proportion of the overall capture cost which is directly attributable to generation of high purity oxygen streams to provide the oxidant for combustion. Outside of the CCP, several organisations are developing the next generation of alternative oxygen separation systems based on ion or oxygen transport membranes. Whilst all of these developments use the principle of high temperature ceramic membranes to separate oxygen from air, there are significant differences between the materials being developed, based on their intended application.

The materials of greatest interest are those which also exhibit electron conductivity, allowing oxygen ions and electrons to move across the membrane without the requirement of an external circuit. The consortia at the forefront of the membrane developments are led respectively by Air Products (developing Ion Transport Membranes or ITMs), Praxair (developing Oxygen Transport Membranes or OTMs) and Alstom/Norsk Hydro (developing Mixed Conducting Membranes or MCMs). All three consortia are targeting commercialisation of the technology around 2008 to 2009.

Ion Transport Membranes in the Oxyfuel Baseline Study

To establish the potential cost reductions available by replacing ASUs with these novel air separation membranes, the CCP worked with Air Products to assess the feasibility of oxyfuel firing the European Refinery scenario. ITM membranes, integrated within a combined cycle gas turbine (CCGT), could provide a source of low pressure air to generate the oxygen for send out to the process users. The membrane configuration assessed by Air Products uses only the partial pressure driving force across the ITM, without any additional sweeping of the permeate side of the membrane. This, together with a need to maintain a suitable level of oxygen for combustion of depleted air in the turbine, limits oxygen extraction across the ITM to around 40% of that present in the incoming air. The basic size of CCGT required to fulfil the O_2 requirements of the refinery scenario is therefore significant, which, coupled with a need to operate the ITMs at high temperatures, set a requirement to generate and export substantial amounts of electricity. The study therefore highlighted that this technology combination is not a good fit for the conversion of the European refinery heaters and boilers, where the absence of a market for the exported power was a limitation, but could be ideally suited for integration with large scale power generation projects.

A range of cases were developed and costed by Air Products[1], although the cost of the basic scheme resulted in a CO_2 avoided cost of $37/tonne. Internal alignment of this cost within the CCP highlighted a range of $25-40/tonne, depending upon the way credit for export power is considered. This represents a saving of at least 20% compared with the cryogenic oxygen production base case. For the other cases developed by Air Products, the CO_2 avoided costs fell in the range $20-30/tonne.

Oxygen Transfer Membranes for New Build Boilers

A further study[3], funded primarily by the U.S. DOE and part-sponsored by the CCP evaluated Praxair's development of the Advanced Boiler (integrating OTMs into new build boilers). The study focused on replacement of a single boiler in the European Refinery scenario with an Advanced Boiler. Whilst the technology is still at an early stage of development, the indicative evaluation by Praxair estimated that the boiler would be around 40% more expensive than a conventional unit. At this early stage of development, it is difficult to quantify the avoided cost of CO_2. Commercialisation of the technology is not expected until around 2010.

The Advanced Zero Emissions Power Concept (AZEP)

A different concept being studied outside of the CCP is being developed by a consortium led by Alstom/Norsk Hydro. The Advanced Zero Emission Power concept (AZEP) is examining the integration of Mixed Conducting Membranes with existing conventional power turbines, targeting complete capture of the CO_2. The CCP commissioned a study with the consortia to examine replacement of gas turbines in the Alaskan scenario.

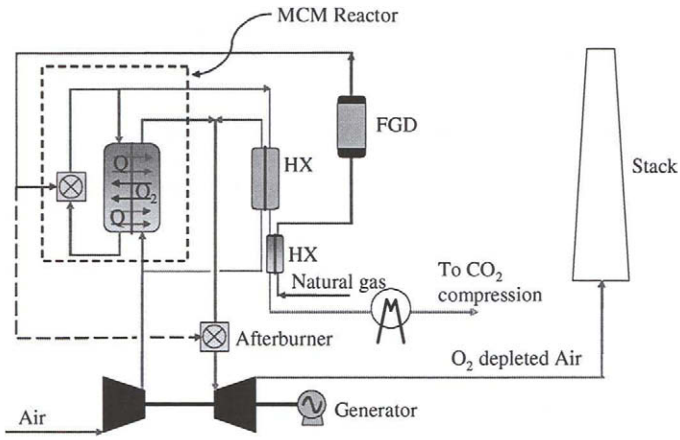

Figure 1: An example of the AZEP Concept

Whilst the turbines selected for study are smaller scale machines (around 45 MW), the AZEP concept is thought to be applicable to much larger CCGT power generation systems. In an attempt to optimise the cost of capture, the CCP study focused on incomplete CO_2 capture (recovering 80-90% of the CO_2) which resulted in a CO_2 avoided cost in the range $25-35/tonne, calculated by Alstom. This represents a significant reduction compared to the Alaska baseline scenario, where the most promising cases have incurred capture costs above $50/tonne for costs developed internally by the CCP. An important aspect of the reduced CO_2 avoided cost is that overall, the AZEP system is more fuel efficient than the baseline system.

It should be noted however that the AZEP concept relies not only on the successful development of Mixed Conducting Membranes, but also on the development of a high temperature heat exchanger, targeted for development during the consortia project. Once again, commercialisation of the technology is expected around 2010.

Boiler Modification Studies

Over the last three years, the CCP has placed a series of studies assessing the potential application of oxyfuel technology specifically to process utility boilers, anticipating that the higher flame temperatures encountered with oxyfuel firing may be more readily managed with boiler systems than with process heaters, as the latter frequently require tighter constraints on combustion characteristics (including flux uniformity and peak flame temperatures).

Two studies were undertaken with Mitsui-Babcock. The first study assessed the concept of a high pressure boiler, where operation of the combustion zone at an elevated pressure may offer the benefits of producing a high pressure flue gas (thereby reducing the requirements for final product CO_2 compression) and an overall reduction in the size and footprint of the boiler system. However, at the optimised operating pressure of 5 bara, potential savings of the system were offset by the increased capital cost of the boiler. The second study assessed the concept of a 'Zero or low recycle oxyfuel boiler', where, for a new build unit, an approach of alternating combustion stages with steam raising tubes along the combustion zone of the boiler may reduce or eliminate the need to recycle flue gas to moderate combustion temperatures. Initial optimisation indicated however, that the requirement to recycle flue gas could not be eliminated and that, in a feasible design, it could only be reduced to 75% of a full recycle system design. Whilst the suggested design resulted in a cost saving of 10% compared with a conventional boiler design, the footprint of such a system was shown to double.

A conceptual study was also undertaken with Praxair[4] to evaluate the option of a new build boiler which employed more exotic materials of construction to eliminate the need to moderate combustion temperatures, anticipating that cost savings may accrue from an overall reduction in equipment size and utility consumption. However, potential savings were more than offset by the increased capital cost. The initial results form all three boiler modification studies suggested these options did not warrant further investigation within the CCP.

Chemical Looping Combustion

The most significant R&D effort in the area of oxyfuel technologies supported by the CCP has been the development of the Chemical Looping Combustion (CLC) concept. Undertaken as a consortium with Chalmers university, Alstom Boilers, Vienna University and CSIC (coordinated by BP), the EU co-funded project has developed a new combustion technology based on using mixed metal oxide pellets as a carrier for transferring oxygen from combustion air to the fuel. The technology utilises two fluidised bed reactors with continuous circulation of solids between the two[5]. The air (1) and fuel (2) reactor systems are shown below in *Figure 2*.

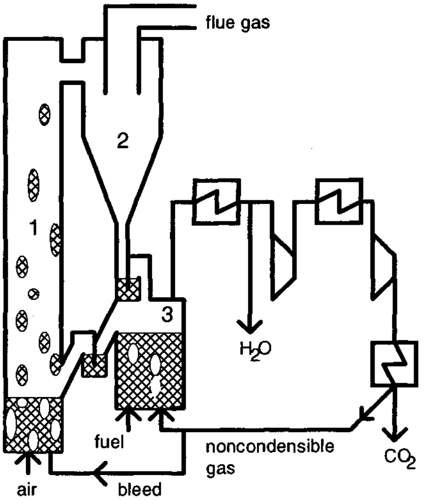

Figure 2: Conceptual schematic of CLC fuel/air reactor

The focus of the current project has been on the application of the technology at atmospheric pressure for a boiler (typical of the European refinery scenario equipment requirements) but the concept is also applicable to higher pressure operation, as already studied for application to gas turbines by a project outside of the CCP.

The key risks associated with the technology development centre on the production of mixed metal oxide materials which are capable of withstanding repeated oxidation/reduction cycles whilst offering a useful level of chemical activity and without suffering undue mechanical damage (attrition). Screening studies performed early on in the project have identified a range of materials suitable for further development. A cold flow fluidised bed unit has been tested to aid design of a pilot unit. This has now been built and operated to demonstrate 'proof of feasibility' which was the main target of the current research efforts. Successful operation of the pilot plant with a Ni-based oxygen carrier has achieved:

- a total of 300 hours of operation, with 100 hours under reaction conditions;
- almost complete Methane combustion (99.5% at 800°C);
- no significant gas leakage between the fluidised beds;
- no significant carbon formation during combustion;
- no significant loss of activity of attrition of the carrier.

In an evaluation undertaken by the CCP (assessing the replacement of a single boiler in the European Refinery scenario), a CLC based boiler was anticipated to offer up to a 43% reduction in the cost of CO_2 capture compared to the Post Combustion baseline study. The next demonstration phase of the technology is anticipated for completion by the end of 2007.

CONCLUSIONS

During the three years of the CCP, a range of oxyfuel technologies have been assessed, ranging from near commercial options to technologies which are not anticipated to be available for commercialisation until the end of this decade. Many of these technologies provide promising opportunities to reduce the cost of CO_2 capture when compared with today's best available technology.

Oxyfuel firing using cryogenically supplied oxygen and flue gas recycle as a means of moderating combustion temperatures has been considered as the 'baseline case' and is considered applicable for retro-fitting to process heaters and boilers at low technical risk, subject to a demonstration of the technology on a commercial scale. The cost of CO_2 capture utilising this option is expected to lie in the range \$35-40/tonne (equivalent to an avoided cost in the range \$40-45/tonne).

The application of pure oxygen firing to gas turbines would require significant development by the turbine manufacturers, incorporating the use of new materials capable of operating at consistently higher temperatures to avoid unacceptable reductions in energy efficiency when the requirements of additional air compression and flue gas recycle are taken into account.

The opportunities for cost reduction offered by a new generation of oxygen production techniques utilising ceramic membrane technologies are attractive and may significantly reduce the unit cost of oxygen production, thereby substantially impacting the cost of CO_2 capture. However, these technologies are still under development and the risks associated with aspects of these developments should not be under estimated.

For the particular oxygen production cycles assessed by the CCP, application of ion transport membranes for retrofit of existing heaters and boilers does not appear overly attractive unless significant markets for exported power exist. Conversely, applied to new build CCGTs or boilers, integration of these membranes looks promising and should be developed further, although the developments are generally at an early stage and the risks to successful commercialisation are still high.

The chemical looping project co-ordinated by the CCP has been very positive from a technical perspective and the risks associated with scale-up of the technology are thought to be reasonable, given the similarity of the operating scheme to conventional circulating fluidised boilers.

REFERENCES

1 Wilkinson M.B., Simmonds M., Allam R.J., and White V., 2003. Oxyfuel Conversion of Heaters and Boilers for CO_2 Capture. *Second National Conference on Carbon Sequestration*, Washington.
2 Simmonds M., Hurst P., Wilkinson M.B., Watt C. and Roberts C.A., 2002. A Study of Very Large Scale Post Combustion CO_2 Capture at a Refining & Petrochemical Complex. *6th International Conference on Green House Gas Control Technologies*, Kyoto.
3 Sirman J.; Thompson D., Switzer L., and Simmonds M., 2004. Oxygen Transport Membranes – An Enabling Technology for Cost Effective CO_2 Capture. *Third National Conference on Carbon Sequestration*, Virginia.
4 Boden J.C., Palkes M., and Thompson D., 2001. A study on CO_2 Capture from a Gas-fired Boiler by Oxyfuel Combustion Without Flue Gas Recycle. *Joint AFRC/JFRC/IEA International Combustion Symposium.*
5 Hurst P., Boden J.C., Wilkinson M.B., and Simmonds M., 2003. Chemical Looping Combustion for CO_2 Capture. *Second National Conference on Carbon Sequestration*. Washington.