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Chemical Looping Combustion for CO_2 Capture

P Hurst, J C Boden, M B Wilkinson and M Simmonds
BP, Sunbury-on-Thames, UK

BP plc
Sunbury on Thames, Middlesex, TW16 7LN, UK
E-mail: Hurstp@bp.com Tel: +44 (0) 1932 775634
E-mail: Wilkinmb@bp.com Tel: +44 (0) 1932 775624
E-mail: SimmonM@bp.com Tel: +44 (0) 1932 775641

Abstract

The CO_2 Capture Project (CCP) and the European Commission are supporting a project by BP (UK), Chalmers University of Technology (Sweden), Consejo Superior de Investigaciones Cientificas (Spain), Vienna University of Technology (Austria) and Alstom Power Boilers (France) to prove the concept of chemical looping combustion technology for boiler applications to facilitate the capture of CO_2. This paper describes the program and its progress. The work runs from January 2002 to December 2003 and covers the development of the particles that will act as oxygen carriers, fluidisation and modelling investigations, study of the design and economics of a future industrial unit and the demonstration of a laboratory-scale chemical looping combustor.

1. Introduction

The CO_2 Capture Project (CCP) is a program of eight international energy companies (BP, EnCana, ENI, ChevronTexaco, Norsk Hydro, Shell, Statoil and Suncor Energy) developing technology to reduce the cost of capturing and storing CO_2 from combustion. The project is funded by the partners and, for different parts of the program, by the European Commission's Framework 5 program, the Norwegian Klimatek program and the US DOE.

The CCP identified and evaluated existing and proposed new technologies for capturing CO_2 from combustion and ranked the proposed technologies for their potential to meet the CCP's targets. The evaluation was carried out in terms of four scenarios, one of which was the capture of CO_2 from a European oil refinery. Among the technologies considered for new-build combustion plant in this scenario, "Chemical Looping Combustion" (CLC) received a high ranking for its potential to reduce CO_2 capture costs and was therefore selected for development as part of the CCP's program.
The project team has been assembled from across Europe, building on previous work by Chalmers University and comprises:
BP, Sunbury, UK
Chalmers University of Technology, Gothenburg, Sweden
Consejo Superior de Investigaciones Cientificas, Instituto de Carboquimica, Zaragoza, Spain (CSIC)
Vienna University of Technology, Austria (TU-Vienna)
Alstom Power Boilers SA, Velizy-Villacoublay, France

2. The Principles of Chemical Looping Combustion

One of the technologies currently proposed for capturing CO_2 is oxyfuel combustion, in which fuel is burnt in oxygen instead of air, thus producing a flue gas consisting mainly of CO_2 and water vapour from which the CO_2 can be readily separated for storage (eg ref 1). Generating oxygen by conventional air separation technology, however, imposes significant cost and energy penalties.

Chemical Looping Combustion is a new technology that, effectively, integrates air separation into the combustion process and achieves the aim of producing a separate CO_2/H_2O flue gas stream for CO_2 capture with an energy penalty that is far lower than for conventional oxygen production. The principle is physically to separate the fuel oxidation process from the air stream by carrying oxygen to the fuel in the form of a metal oxide. In oxidising the fuel in a "fuel reactor" the metal oxide is reduced to a lower oxide state or, ultimately, to the metal itself. This is transported to an "air reactor" where it is re-oxidised 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.

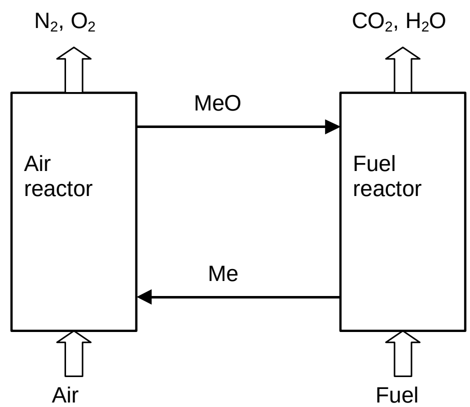

Figure 1. Principle of chemical looping combustion (MeO = metal oxide)

Groups in Japan (eg ref 2), Sweden (eg ref 3), the USA (eg refs 4, 5) and elsewhere have tested metal oxide systems in the laboratory and have modelled the process. The favoured design for boiler applications uses fluidised beds for the fuel and air reactors. The proposed layout is analogous to a circulating fluid bed boiler, in which the air reactor is a fast fluidised bed or transport reactor and the fuel reactor, which requires a lower gas flow, is a bubbling bed. A typical arrangement is shown in Figure 2 (from ref 3).

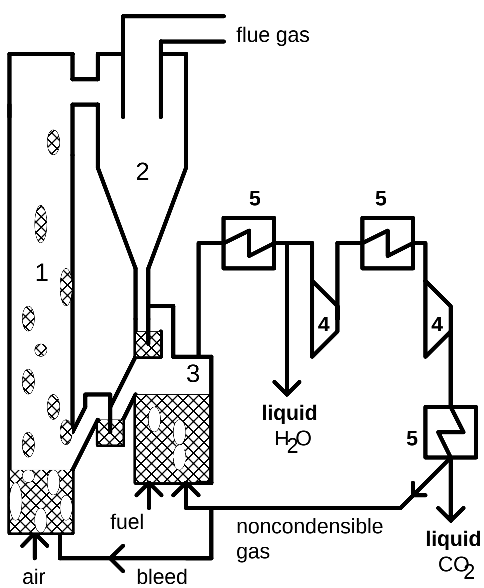

Figure 2. Schematic layout of chemical looping combustor excluding flue gas heat recovery (1. Air reactor. 2. Cyclone. 3. Fuel reactor. 4. Compressors. 5. Heat exchangers)
Schematic courtesy of Chalmers University.

For the metal/metal oxide systems considered, most or all of the exothermicity occurs in the air reactor. Therefore the heat of combustion will be recovered mainly from the air reactor and from the oxygen-depleted air stream from this reactor.

Most previous studies have been aimed at gas turbine power generation systems, in which the chemical looping combustor would be operated at elevated pressure and the hot depleted air from the air reactor would be passed to the turbine. In order to achieve power generation efficiencies comparable to the best conventional plant, the chemical looping system would need to operate at temperatures which provide a severe challenge for the carrier particles, or the temperature of the depleted air would need to be boosted by adding further fuel, giving rise to some CO_2 emission.

The present program is aimed at a different application, that of gas-fired industrial boilers. Here the system can operate at near to atmospheric pressure and the temperatures will be limited to those used in conventional circulating fluidised bed boilers, which are typically in the region of 850°C to 900°C.

In order to meet the requirements of the CCP's European Refinery Scenario, the target for the development is one of the boilers at the example refinery. This is a 200 MW (fired duty) unit producing 227 tonne/hour of superheated steam for co-generation of power and process steam. Refinery gas and natural gas are the specified fuels.

3. GRACE Project

The full project title is the Grangemouth Advanced CO_2 Capture Project (GRACE).
The project is jointly funded by the European Commission, under the Framework 5 program, and by the CCP (Carbon dioxide Capture Project) and has a programme budget of €1.49 million (Euro) for the Chemical Looping Combustion element of the programme.
The project was developed to take Chemical Looping Combustion technology to the proof of concept stage over a period of two years from January 2002 to December 2003.
The program has two main targets:

- to demonstrate a laboratory chemical looping combustor with metal oxide particles which have adequate reactivity and lifetime for an economically acceptable commercial system to be projected. The performance of the particles will be critical to the success of the technology.

- to develop an outline design and economic analysis for an industrial plant based on the refinery boiler described above.

To achieve these objectives the work was broken down into five packages, coordinated by BP and its CCP partners:

1. Particle development and screening tests (CSIC and Chalmers)
2. Comprehensive testing of carrier materials (CSIC and Chalmers)
3. Fluidisation Conditions (TU-Vienna)
4. Construction and testing of CLC unit (Chalmers)
5. Design criteria and Industrial Scale-up (Alstom)

3.1 Particle Development

The particles will consist of transition metal oxides to provide the reactivity and support materials to provide the required physical properties.
For screening purposes all possible combinations between metal oxides (CuO, Fe_2O_3, MnO_2, NiO) and inerts (Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2) with three MeO/inert ratios at different sintering temperatures and manufacturing techniques were prepared. Reactivity characterisation was carried out by thermogravimetric analysis (TGA) at temperatures from 800 to 950ºC using CH_4/H_2O mixtures for reduction and air for oxidation. These tests analyse the effects of the structural changes produced in the particles as a consequence of the successive reduction and oxidation reactions of the metal oxide present in the particle. Laboratory fluidised bed multiple cycles in similar conditions were used to consider both the structural changes as a consequence of the chemical reaction, and the agglomeration and attrition phenomena existing in a fluidised bed. Approximately 250 different types of particle were made and screened during the first year of the project. As an example, Figure 3 shows the reduction and oxidation behaviour of copper particles Cu 4095 during multiple cycles (5, 25, 50 and 100 cycles). Screening was made considering reactivities in both oxidation and reduction and fluidised bed behaviour and by standard techniques for physical properties including crushing strength.

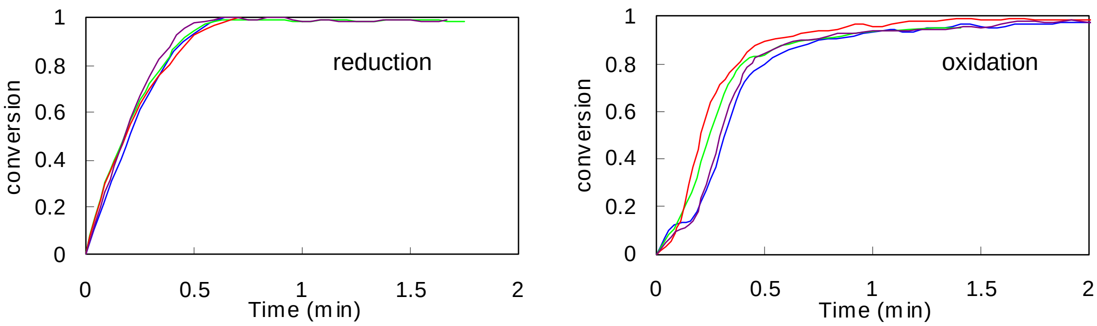

Figure 3. Conversion vs time of Cu4095 particles during multiple cycles at TGA.

During the second year of the program the best of these will be selected to undergo detailed testing by TGA and in laboratory fluid beds to determine the kinetics over a wider range of operating variables and particle sizes, both for optimisation purposes and as input to process modeling, and to produce additional data on particle integrity. In addition, the selected particle types will be the basis of larger batches of particles to be manufactured for testing in a laboratory chemical looping combustor.

3.2 Fluidisation Conditions

A major input to the design of the laboratory chemical looping combustion rig and to the industrial plant outline design has come from a series of cold flow models of the circulating particle system. These have been built and tested during the first year of the project.
A cold flow model based on a modular concept (**Figure 4**) was chosen for the laboratory test rig. This approach permitted the evaluation of the fluid dynamic behaviour of the reactor system and the study of the effect of design variations.
A number of parameter studies and configuration changes were undertaken with the major objectives of optimising the solids transport and gas mixing, minimising by the use of loop seals between the reactors, and determining acceptable operating ranges in terms of gas velocities and particle properties.

Figure 4. Photograph of chemical looping combustor cold flow model
(1. Air reactor. 2. Riser. 3. Particle separator. 4. Loop seal. 5. Fuel reactor)

A cold flow model for an industrial scale CLC unit has been developed by this project and has been used to demonstrate the functionality of the proposed reactor system for large scale units.
In conjunction with this work a mathematical description of the circulating particle system has been developed. The relationships obtained experimentally, and from simulation work, will allow the derivation of scale-up criteria from the laboratory test rig to full-scale CLC units.

3.3 Laboratory Chemical Looping Combustion Unit

A key aspect of the proof of concept will be the successful demonstration of a chemical looping combustor. The unit for laboratory testing has been designed to be as flexible as possible in terms of the particle reactivity, since the particles chosen for development vary in this respect, and will accept defined ranges of particle sizes, recirculation rates, bed inventories and temperatures. The scale of the unit has been chosen to have a heat output of 5-10 kW to allow it to be accommodated within the laboratory facilities. Construction of this unit is now complete and the first tests are under way.

3.4 Industrial Plant Design and Scale-up Criteria

In order to carry out an economic and preliminary feasibility assessment of chemical looping combustion as applied to the CCP Refinery Scenario, Alstom Power Boilers are preparing an outline design of a CLC boiler to match the output of the baseline 200MW (fired duty) boiler at the selected refinery. The work includes the main process flow diagrams, process design calculations, equipment sizing and layout and estimates of capital and operating costs. Alstom's experience in the design and construction of circulating fluidised bed boilers with a very similar layout to the proposed CLC design has given increased confidence in the feasibility of the design approach.

3.5 Safety and Environmental Aspects

Safety and environmental aspects of the proposed design are being reviewed throughout the program, particularly with respect to the selection of particle materials and the minimisation of emissions.

4. Conclusions, Key Challenges and Future Development

The chemical looping combustion project described in this paper is on schedule to deliver proof of concept for an industrial boiler application by the end of 2003. This will be achieved through a ~10 kW laboratory unit and an economic and preliminary feasibility assessment of an industrial boiler application. The development of this technology can take advantage of ongoing developments in CFB technology and appears suitable for a rapid transition to a demonstration stage.

A preliminary costing carried out by the CCP indicates that the CO_2 capture cost could be substantially below that of existing capture technologies if the targeted particle performance is achieved.

The long term performance of the metal oxide particle systems is the key challenge for the technology. These particles need to demonstrate;

- a robust and long service life.
- low cost.
- sound environmental performance.

Given a successful outcome to this project, future development should centre on intensive particle development and long term proving, together with demonstration at the pilot scale, probably in the 1-10 MW range

5. Acknowledgements

The contributions of all the partners in this collaborative project and the support of the European Commission's FP-5 program and of the CO_2 Capture Project are acknowledged.

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