

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Capture and Separation of Carbon Dioxide
from Combustion Sources**

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Volume 1



ELSEVIER

2005

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First edition 2005

Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

British Library Cataloguing in Publication Data

A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

Volume 1: Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

Volume 2: The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

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Chapter 27

ZERO RECYCLE OXYFUEL BOILER PLANT WITH CO₂ CAPTURE

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ABSTRACT

The Carbon Capture Project has been established by eight leading energy companies to develop novel technologies that significantly reduce the cost of capturing CO₂ for long-term storage. One area considered by the CCP is the use of oxygen in combustion systems (oxyfuel combustion). This is attractive to the CCP as it produces a flue gas essentially containing only CO₂ and water, from which CO₂ can be easily captured.

This study reviews two oxyfuel schemes, one that incorporates a recycle of some of the flue gas and one that does not. Recycling a proportion of the flue gas helps to mitigate the combustion temperatures in the furnace and thereby permit the use of conventional boiler designs. Eliminating the flue gas recycle and burning fuel gas in a near-pure oxygen environment is beneficial as it leads to a more thermally efficient and thereby compact boiler design, and has a lower volumetric throughput, thus reducing the size of all equipment and ducting. Very high temperatures are reached in the zero recycle case and novel boiler design are required. This study evaluates the technical feasibility of the zero recycle case and assesses the justification for developing new boiler designs as part of the CCP.

The study concludes that the zero recycle scheme is technically feasible. A boiler design is proposed that is capable of withstanding the high combustion temperatures but, although such a design has been tested in a pilot study, it is not currently commercially proven.

The zero recycle case is an attractive option for raising steam and generating electrical power. It is cheaper than the alternative scheme that does recycle part of the flue gas and, for identical feed conditions, generates more electrical power. However, both cost- and thermal-efficiency benefits are only marginal and it is concluded that there is insufficient justification to warrant the development of boiler designs suited to fuel gas combustion in a near-pure oxygen environment within the CCP.

INTRODUCTION

The CO₂ Capture Project (CCP) is a joint project being undertaken by eight major energy companies to develop new and novel technologies that significantly reduce the cost of capturing and storing CO₂. The project is split into three distinct elements:

- pre-combustion de-carbonisation,
- the use of oxygen-rich combustion systems, and
- post-combustion CO₂ recovery.

For each element, technologies will be developed in the context of certain scenarios that relate to combustion sources and fuels common to the operations of the CCP participants. Four scenarios are considered:

- large gas-fired turbine combined cycle power generation,
- small or medium sized simple cycle gas turbines,

- petroleum coke gasification, and
- refinery and petrochemical complex heaters and boilers.

This report details a study to evaluate the potential benefits of developing novel boiler designs that are suitable for use in high purity oxygen-based combustion systems.

Oxyfuel combustion is attractive to the CCP as it produces a flue gas consisting largely of carbon dioxide and water, from which CO₂ can be easily separated. The main problem with oxyfuel systems, other than the supply of oxygen, is the combustion temperature, which is far above that reached with conventional air-fired systems. Recycling some of the flue gas to act as a diluent and thereby help to moderate combustion temperatures is one option to manage this problem. Such a solution allows the use of conventional boiler plant design with only minor modifications, but introduces a cost penalty caused by the addition of a recycle flue gas blower and ducting, and the need for larger equipment to cope with higher gas throughputs.

Using oxygen alone to fire the combustion process eliminates the flue gas recycle and will lead to inherently smaller equipment as the gas throughput is lower. In addition, generating higher temperatures and thereby higher heat fluxes in the boiler increases the thermal efficiency and permits more compact boiler design. Unfortunately, as yet such a boiler design is not commercially available, although a Japanese consortium has conducted a full-scale pilot test that demonstrated the technical feasibility of an oxygen-fired boiler.

The aim of this study is to assess the feasibility of an oxyfuel combustion system without flue gas recycle. Furthermore, this study compares the installation costs of oxyfuel systems with and without flue gas recycle and on this basis assesses the justification for developing boiler designs, for use with high purity oxygen, through to commercialisation.

This study work was commissioned by the CCP and co-ordinated by BP. Technical evaluation and process scheme costing was undertaken by Alstom Power Inc. and Praxair Inc.

EXPERIMENTAL/STUDY METHODOLOGY

Study Methodology

Two rival oxyfuel system designs are considered by this study—one incorporating flue gas recycle and near conventional boiler design, and the other without flue gas recycle and novel boiler design. For each system:

- A process schemes is proposed,
- Boiler designs are considered and a suitable option proposed,
- Air separation and CO₂ recovery processes are selected, and
- An installed capital cost estimate to order of magnitude (OOM) accuracy has been developed.

This then allows the performance of each option to be evaluated and conclusions drawn as to the justification for developing novel boiler designs for use in the zero recycle case.

Design Basis

The basis of design for both oxyfuel systems is as follows:

- Boiler thermal capacity is 223 MW,
- Boiler to be fired by natural gas with the composition given below:

Methane	98.42 wt%
Nitrogen	1.04 wt%
Carbon dioxide	0.54 wt%
HHV	23,518 Btu/lb (or 54.7 MJ/kg)

- Furnace to have fusion welded walls. An induction draft fan is not required,
- The steam generated in the boilers is to be applied to generate electrical power only—no process steam demand is assumed,
- Steam generated in the boiler is superheated to meet the following conditions:

Pressure 1350 psig (92.8 bar)
 Temperature 950 °F (510 °C).

- Ambient conditions are as follows:

Temperature 80 °F (26.7 °C)
 Pressure 14.7 psi (1.01 bar)
 Relative humidity 60%
 Cooling water supply temperature 80 °F (26.7 °C)
 Maximum CW temperature rise 15 °F (8.3 °C)

- CO₂ to be delivered at a pressure of 1450 psig (99.7 barg), and with a purity of at least 97 wt%.

The scope of each system to include:

- Boiler-steam turbine sub-system,
- Air separation unit,
- CO₂ separation and compression.

RESULTS AND DISCUSSION

This section details the oxyfuel schemes considered by the study and summarises both the performance and installed costs of each.

Oxyfuel Combustion System Process Descriptions

Two process schemes are considered:

- Oxyfuel combustion *with* flue gas recycle shown in Figure 1;
- Oxyfuel combustion *without* flue gas recycle shown in Figure 2.

A brief process description of each option is given in this section.

Oxyfuel combustion system with flue gas recycle [2]

A schematic of this option is given in Figure 1.

Natural gas (stream 1) is fired in the steam generator unit, where the heat of combustion is released and transferred to the boiler waterwalls, superheater and economiser heat transfer surfaces (note that these are within the “steam generator unit” block in the above diagram).

Flue gas leaving the boiler (stream 2), is cooled further to below its dew point in a second, low-temperature economiser and a gas cooler. The low-grade heat removed between streams 2 and 4 in the above diagram is partially recovered by heating condensate from the steam turbine (stream A) before that condensate is then fed to the deaerator (stream B). The balance of the heat removed between streams 2 and 4 (approximately 72.5 MMBtu/h) is rejected to atmosphere. Condensed water is removed from the low-temperature economiser and directed to a water treatment plant (not shown above).

The cooled flue gas (stream 4) is then split into two streams—a flue gas recycle (stream 6) and an exhaust stream (stream 5). The recycle gas is mixed with combustion oxygen supplied by a conventional cryogenic

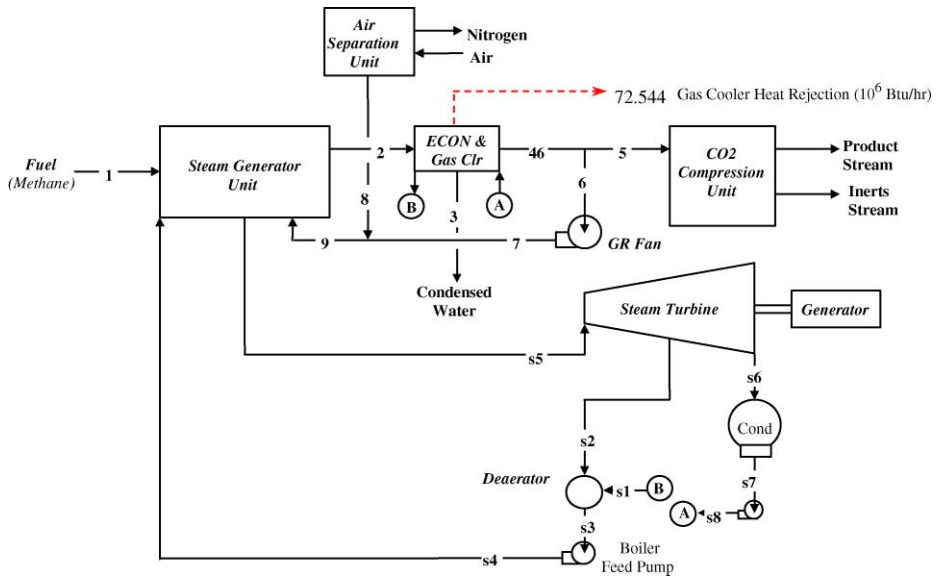


Figure 1: Process design for an oxyfuel boiler with flue gas recycle.

air separation unit. The oxygen-flue gas mixture is then routed to the furnace for combustion. Flue gas recycle flow rate is sufficient to reduce the oxygen content of the combined stream to the furnace (stream 9) to about 21 mol%, i.e. similar to the oxygen content of air.

The exhaust flue gas stream (stream 5) is fed to the CO₂ separation and compression unit where CO₂ is separated from any inerts (e.g. residual oxygen, CO and nitrogen-based components) and then compressed to 1450 psig (99.7 barg).

Steam generated in the boiler (the “steam generator unit” above) is expanded through a steam turbine to produce electrical power. At full load operation and assuming a boiler thermal capacity of 223 MW, this option will generate approximately 58.3 MW of electrical power, equating to a thermal efficiency of 25.1%. In addition, 914 mtpd of CO₂ will also be produced.

Oxyfuel boiler with zero flue gas recycle

The schematic of this option is shown in Figure 2.

The process scheme is very similar to that outlined above, except that in this case, natural gas is burnt in oxygen without the diluting effect of the flue gas recycle. Consequently, the temperature of combustion is much higher, the heat flux is much increased and the flue gas flow rate is much lower (approximately 26 vol% of the previous case). The water content of the flue gas in stream 3 above is much higher than the corresponding stream in the previous case, thus raising the dew point and allowing much higher levels of heat recovery from the condensing water vapour. This increase in the heat recovery from the low-temperature economiser is the main factor boosting the power generation of this option to 60.1 MW at full load, giving a thermal efficiency of 25.9%. CO₂ production from this option is approximately 903 mtpd.

Neither of the process schemes proposed above have been optimised to improve thermal efficiency. The first case considered (including flue gas recycle) could be optimised to achieve a similar thermal efficiency to the zero recycle case, but would require a more complex heat recovery process and additional equipment.

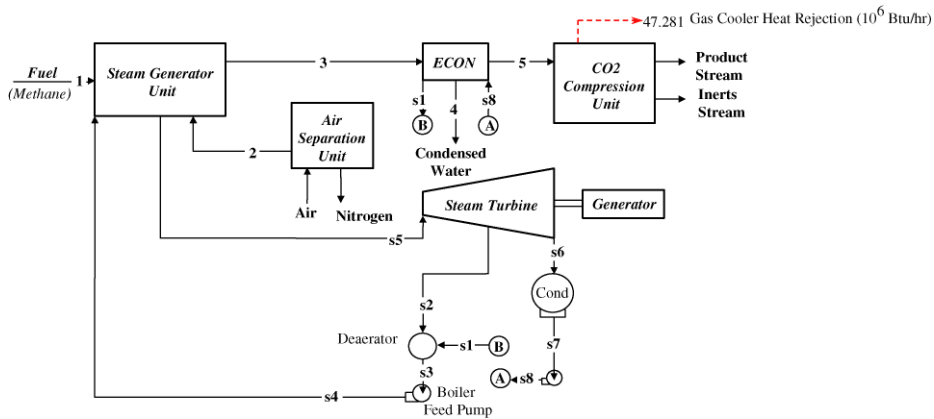


Figure 2: Process design for an oxyfuel boiler with zero flue gas recycle.

Oxyfuel Boiler Subsystem

This section discusses the boiler design for the two schemes outlined previously. Boiler designs for both options are derived from a conventional industrial steam generator, in which, the furnace is pressurised and combustion air is pre-heated. The furnace walls are water-cooled and are constructed of panels formed by 2.5 in. OD finned tubes. Waterwalls are constructed of carbon steel alloy. The tubes are cooled by a circulating water/steam mixture and capture a large share of the heat liberated by the natural gas combustion. Adequate circulation of the water/steam mixture is essential to retain a nucleate boiling regime and avoid exceeding the tube design temperature limit.

As the flue gas leaves the furnace, it is cooled by the superheater tubes located both above the furnace and in the back-pass. Typically, the superheater tubes are constructed of carbon steel and low chrome (<1.5%) ferritic steel alloys. Downstream of the superheater section in the back-pass, an economiser preheats the boiler feedwater. Typically, the economiser is constructed of carbon steel.

Oxyfuel boiler with flue gas recycle

The design of the oxyfuel boiler with flue gas recycle closely resembles the conventional design as shown in Figure 3.

As mentioned previously, the ratio of recycle flue gas to the oxygen feed is similar to the ratio of nitrogen to oxygen contained in conventional combustion air. Consequently, the heat flux across the heat transfer areas and the temperatures generated are similar, thus permitting similar materials of construction—in fact the heat flux is slightly higher than the conventional design due to the higher levels of water vapour and CO₂ in the combustion products, which, in turn, allows a slightly more compact boiler design to be possible reducing the overall furnace and superheater heat transfer areas by about 10%.

The economiser is split into two section, one inside the back-pass and one in the downstream ducting (note only the latter section is shown in the schematic in the previous sub-section). Both sections combine to pre-heat the boiler feed water and in so doing, reduce the flue gas temperature to about 100 °F (37.8 °C). Both economiser sections are constructed of stainless steel.

Oxyfuel boiler with zero flue gas recycle [1]

Combustion of natural gas in an oxygen environment with zero flue gas recycle has a significant impact on boiler design. Combustion temperatures in this case may approach 5000 °F (2760 °C), generating very high heat fluxes in the furnace. In addition, the quantity of flue gas produced is an OOM smaller than in the flue

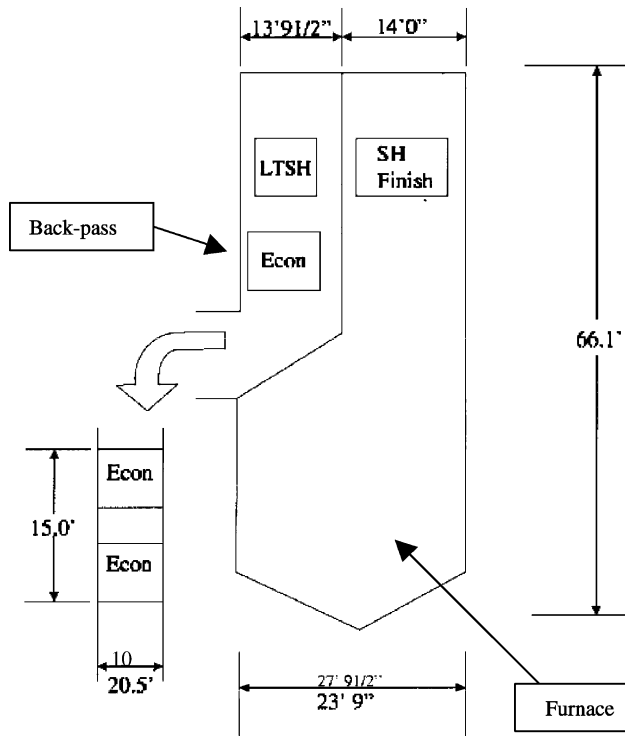


Figure 3: Conventional boiler design modified for flue gas recycle oxyfuel service.

gas recycle case or the conventional design (approximately 26% of the throughput). Both high combustion temperature and reduced flow rate impact the surface arrangement and the materials of construction. A schematic of the proposed boiler design is given in Figure 4.

The high temperature of combustion produces a high heat flux that may be in excess of 325,000 BTU/hft² (1025 kW/m²). This is much higher than experienced in current commercial designs and produce a design, which has significantly less furnace surface area than the recycle flue gas option above. However, to accommodate high heat fluxes, more expensive low chrome (1.5%) ferritic alloy materials are required for the waterwall tubes. Whilst this alloy is conventionally used in large utility boilers designed for supercritical pressures, it is more expensive than carbon steel tubing.

The high heat fluxes also lead to a large temperature differential over the tube walls in excess of 200 °F (111 °C). A preliminary review indicates that this does not create unacceptable hoop stress levels within the tubing, however, a more detailed stress analysis of the waterwall tubing is required to assure the structural integrity of the furnace walls.

Finally, the high furnace heat flux may have an impact on the boiling regime within the waterwall tubes. A cursory analysis indicates that the zero flue gas recycle case will operate in the nucleate boiling regime, but a more detailed analysis of the circulation system is required to verify that this is the case.

In addition to the impact on the furnace waterwall tubes, the superheater design is also greatly affected when combustion is in near-pure oxygen conditions. The smaller flue gas flow rate leads to the superheater being installed in a zone of the boiler that is at a much higher temperature—a gas inlet temperature of approximately

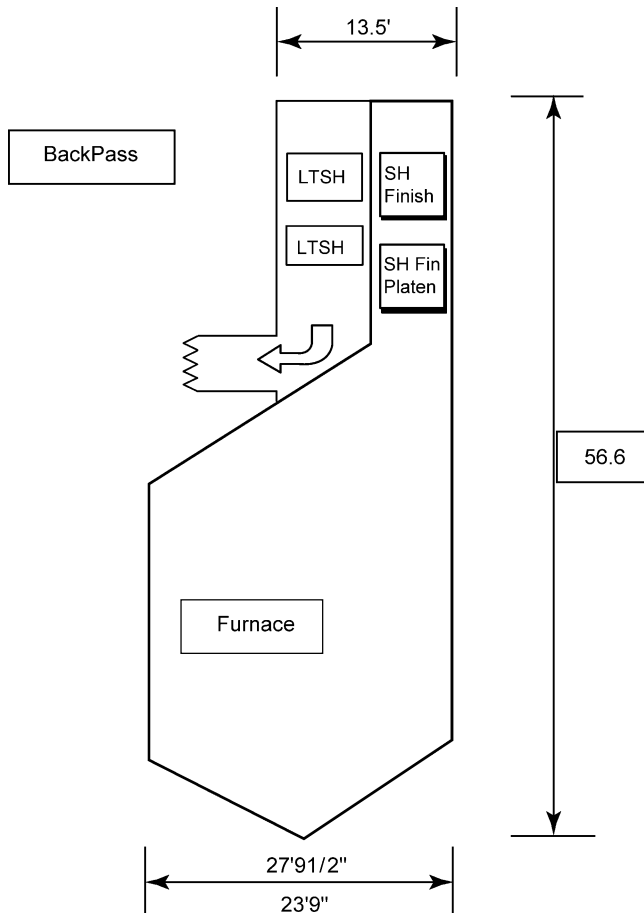


Figure 4: Conventional boiler design modified for zero recycle oxyfuel service.

3000 °F (1649 °C) and a gas exit temperature of about 725 °F (385 °C). The convective surface tunnels, over the furnace and in the back-pass, where the superheater surfaces are located, are reduced in width to maintain a high velocity of the flue gas flowing over the tubes and to facilitate effective heat transfer. Due to the higher inlet gas temperature, it is necessary to select a higher strength alloy (9% Cr steel).

The economiser is again constructed of stainless steel and is similar in design to the previous boiler design case.

Air Separation Plant (ASU)

Both process schemes considered in this study require a supply of oxygen. Conventional cryogenic technology is selected to separate oxygen from air, consisting of:

- air compression,
- adsorption of impurities such as water and CO₂,
- refrigeration of the purified air stream,
- fractionation into oxygen- and nitrogen-rich streams.

Two levels of oxygen purity are considered—a low-purity option containing approximately 95.5 mol% of oxygen and a high-purity option with approximately 99.5 mol% oxygen. The cost and performance of both options, each sized to meet the demands of the oxyfuel schemes considered, is summarised in Table 1.

TABLE 1
COMPARISON OF OXYGEN PURITY OPTIONS FOR OXYFUEL FIRING
OF BOILERS

	Low purity	High purity
Oxygen purity (mol%)	95.5	99.5
Oxygen production (tonnes/day)	1900	1900
Oxygen pressure (psig)	5	5
Power demand (MW)	16.3	19.4
Capital cost (\$MM)	26	27.5

Note that the power consumption of the low-purity ASU can be further reduced by 1.5 MW if the oxygen supply pressure can be reduced to 1 psig.

The choice of ASU design is dependent not only on Table 1 but also on the cost and performance of the CO₂ separation and compression unit. Selecting the low-purity oxygen supply option will lead to an ASU lower cost and power demand, but will also introduce more inerts (nitrogen) into the combustion system, and thereby into the flue gas. Consequently, the throughput of the CO₂ compression unit is slightly higher. Selection of the ASU design is therefore undertaken with due consideration of the cost and power demand impact on the CO₂ separation and compression unit. This is covered in “Carbon Dioxide Separation and Compression Unit”.

Carbon Dioxide Separation and Compression Unit

The process selected to separate CO₂ from other components in the flue gas is fairly conventional. The flue gas stream entering the separation stage is first cooled via direct contact with water. Water removed from this cooler will contain some level of CO₂ and may be slightly acidic. An alkaline scrubber can be included to control the water pH if necessary, although from a cost perspective, this has not been adopted in this case. Once cooled, the flue gas is compressed in a multi-stage compressor to about 23.5 barg, and then dried in an alumina-based adsorption bed. The dry, compressed, impure CO₂ stream is then cooled below the dew point (to about -55 °F or -48 °C) and separated into two streams—a liquid CO₂-rich stream and a gaseous inert-rich stream (mainly nitrogen). The CO₂-rich liquid stream is then re-heated by heat exchange with the cooling impure CO₂ stream and then compressed to 100 barg.

In addition to the above process configuration, a membrane can also be used to recover CO₂ upstream of the refrigeration section, thus reducing the refrigeration load.

As noted in the previous section, the level of impurities present in the oxygen supply has an impact on the capital cost and power demand of the CO₂ separation and compression unit. Four cases have been considered:

- (i) A low-purity oxygen ASU design, coupled with an oxyfuel scheme with flue gas recycle,
- (ii) A low-purity oxygen ASU design, coupled with an oxyfuel scheme without flue gas recycle,
- (iii) A low-purity oxygen ASU design, coupled with an oxyfuel scheme without flue gas recycle and a CO₂ separation unit incorporating a membrane pre-separator,
- (iv) A high-purity oxygen ASU design, coupled with an oxyfuel scheme without flue gas recycle.

The performance and cost of these four systems is summarised in Table 2—note that the cost and power demand of the ASU design is included.

Based on the above results, the low-purity oxygen supply is selected for both oxyfuel schemes, i.e. both with and without flue gas recycle.

TABLE 2
COMPARISON OF OXYFUEL COMBUSTION WITH AND WITHOUT FLUE GAS RECYCLE AND OXYGEN PURITY OPTIONS

Case number	(i)	(ii)	(iii)	(iv)
<i>ASU</i>				
Power demand (MW)	16.3	16.3	16.4	19.4
Capital cost (\$MM)	26	26	26	27.5
<i>CO₂ separation and compression unit</i>				
Power demand (MW)	5.9	5.9	6.2	5.6
Capital cost (\$MM)	5.75	5.78	6.25	5.63
Total power demand (MW)	22.2	22.2	22.3	25.0
Total capital cost (\$MM)	31.7	31.7	32.2	33.1
Captured CO ₂ (mtpd)	914	903	955	974

Plant Performance

A comparison of the performance of the two oxyfuel combustion schemes considered is given in Table 3.

TABLE 3
COMPARISON OF OXYFUEL COMBUSTION PLANTS WITH FLUE GAS RECYCLE OPTIONS

Oxyfuel case	With flue gas recycle	With zero flue gas recycle
Fuel fired (MW)	232	232
Gross generator output (MW)	80.9	82.6
Net generator output (MW)	58.3	60.1
Net plant heat rate (Btu/kWh)	13612	13208
Net plant efficiency (%)	25.1	25.9
CO ₂ recovered (mtpd)	914	903

As indicated in Table 3, under identical conditions, the zero recycle case generates approximately 2 MW of additional electrical power. The primary reason for this is the additional heat recovered from the economiser downstream of the steam generator unit.

Note that the estimated plant efficiencies include power consumed by the low-purity oxygen plants, CO₂ separation and compression unit, gas re-circulation blowers (where applicable), boiler feed water pumps and cooling water pumps.

Cost Estimates

Cost estimates for the two oxyfuel combustion schemes are outlined in Table 4.

The cost for the boiler-steam turbine unit for the case *with* flue gas recycle is based on a capital cost of \$550 per kilowatt of gross generator output. The equivalent cost for the *zero* recycle case has been pro-rated from this baseline using appropriate cost factors and adjustments.

Although the costs are fairly high, the cost of installing the zero recycle design per kilowatt of generated power is approximately 4.5% lower.

TABLE 4
COST ESTIMATES FOR OXYFUEL COMBUSTION WITH AND WITHOUT FLUE GAS
RECYCLE

Oxyfuel case	With flue gas recycle	With zero flue gas recycle
Installed capital cost (\$MM)		
Boiler-steam turbine	44.5	43.2
ASU	26	26
CO ₂ Separation and compression unit	5.7	5.8
<i>TOTAL</i>	76.2	75.0
Net power output (MW)	58.3	60.1
Capital cost per MW (\$)	1.31	1.25

For reference, the accuracy of the boiler-steam turbine cost estimate is approximately $\pm 40\%$, although given the additional factors and adjustments made to the ZERO recycle case, its cost estimate will have a slightly lower accuracy than the recycle case. Cost estimates for the ASU and CO₂ separation/compression units are slightly better and are considered to be to an accuracy of $\pm 25\%$.

CONCLUSIONS

The conclusions drawn from this study are as follows:

1. An oxyfuel combustion scheme incorporating ZERO flue gas recycle is technically feasible with the following caveats relating to the furnace design:
 - A detailed stress analysis of the waterwall tubing is required to assure structural integrity of the furnace walls in the light of the higher heat flux that will occur with combustion in a near-pure oxygen environment.
 - A detailed analysis of the water/steam circulation system is required to verify that the a nucleate boiling regime predominates.

An oxyfuel combustion scheme with zero flue gas recycle has not, however, been commercially proven.
2. An oxyfuel combustion scheme for generating steam and capturing CO₂ incorporating ZERO flue gas recycle marginally outperforms a rival scheme with flue gas recycle on the basis of a lower installed capital cost and a higher thermal efficiency.
3. Even though the zero recycle case is marginally cheaper and generates slightly more electrical power than the flue gas recycle option, there is insufficient justification to warrant the development of a boiler design capable of handling the temperatures generated by the combustion of a typical fuel gas in a near-pure oxygen environment.

NOMENCLATURE

ASU	air separation unit
CCP	CO ₂ Capture Project
CW	cooling water
ECON	economiser
GR	gas recycle
HHV	higher heating value
LTSH	low-temperature super heat
Mtpd	thousand tonnes per day
MW	mega watt
OD	outside diameter
OOM	order of magnitude
SH	super heat

ACKNOWLEDGEMENTS

The authors would like to acknowledge the work of Alstom Power Inc. and Praxair Inc., upon which this chapter is based.

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