Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

Edited by

David C. Thomas
Senior Technical Advisor
Advanced Resources International, Inc.
4603 Clearwater Lane
Naperville, IL, USA

Volume 1

ELSEVIER
2005

Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

Elsevier Internet Homepage – http://www.elsevier.com
Consult the Elsevier homepage for full catalogue information on all books, major reference works, journals, electronic products and services.

Elsevier Titles of Related Interest

AN END TO GLOBAL WARMING
L.O. Williams
ISBN: 0-08-044045-2, 2002

FUNDAMENTALS AND TECHNOLOGY OF COMBUSTION
F. El-Mahallawy, S. El-Din Habik
ISBN: 0-08-044106-8, 2002

GREENHOUSE GAS CONTROL TECHNOLOGIES: 6TH INTERNATIONAL CONFERENCE
John Gale, Yoichi Kaya
ISBN: 0-08-044276-5, 2003

MITIGATING CLIMATE CHANGE: FLEXIBILITY MECHANISMS
T. Jackson
ISBN: 0-08-044092-4, 2001

Related Journals:
Elsevier publishes a wide-ranging portfolio of high quality research journals, encompassing the energy policy, environmental, and renewable energy fields. A sample journal issue is available online by visiting the Elsevier web site (details at the top of this page). Leading titles include:

Energy Policy
Renewable Energy
Energy Conversion and Management
Biomass & Bioenergy
Environmental Science & Policy
Global and Planetary Change
Atmospheric Environment
Chemosphere – Global Change Science
Fuel, Combustion & Flame
Fuel Processing Technology

All journals are available online via ScienceDirect: www.sciencedirect.com

To Contact the Publisher
Elsevier welcomes enquiries concerning publishing proposals: books, journal special issues, conference proceedings, etc. All formats and media can be considered. Should you have a publishing proposal you wish to discuss, please contact, without obligation, the publisher responsible for Elsevier's Energy program:

Henri van Dorssen
Publisher
Elsevier Ltd
The Boulevard, Langford Lane
Kidlington, Oxford
OX5 1GB, UK

Phone: +44 1865 84 3682
Fax: +44 1865 84 3931
E.mail: h.dorssen@elsevier.com

General enquiries, including placing orders, should be directed to Elsevier's Regional Sales Offices – please access the Elsevier homepage for full contact details (homepage details at the top of this page).

ELSEVIER B.V.
Radarweg 29
P.O. Box 211, 1000 AE Amsterdam
The Netherlands

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego, CA 92101-4495
USA

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London WC1X 8RR
UK

© 2005 Elsevier Ltd. All rights reserved.

This work is protected under copyright by Elsevier Ltd, and the following terms and conditions apply to its use:

Photocopying
Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: permissions@elsevier.com. Requests may also be completed on-line via the Elsevier homepage (http://www.elsevier.com/locate/permissions).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works
Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage
Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.
Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

Notice
No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

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.

♾ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).
Printed in The Netherlands.

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER BOOK AID International Sabre Foundation

Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1
D.C. Thomas and S.M. Benson (Eds.)

Chapter 32

COST AND FEASIBILITY STUDY ON THE PRAXAIR ADVANCED BOILER FOR THE CO_2 CAPTURE PROJECT'S REFINERY SCENARIO

Leonard Switzer, Lee Rosen, Dave Thompson, John Sirman, Hank Howard and Larry Bool
Praxair, Inc., Tonawanda, NY, USA

ABSTRACT

Praxair, Inc. has developed a preliminary design and cost estimate for a boiler system that uses Praxair's advanced boiler technology to produce product steam, a system to capture the CO_2 from the boiler exhaust. This report is in response to the Carbon Capture Project's refinery scenario. A model has been developed for an advanced boiler that combusts a gaseous fuel with O_2, which is supplied from a thermally integrated network of oxygen transport membranes (OTMs). The exhaust from this system—being primarily CO_2 and water—is then purified and compressed to recover the CO_2 as a product. The OTMs are in the form of tubes arranged perpendicular to the direction of the exhaust gas flow in the furnace. Air circulated inside the membranes provides oxygen for combustion. As O_2 is transported through the membrane, it combusts with the fuel and creates the required oxygen partial pressure gradient through the tube wall to facilitate transport. The heat release from the combustion keeps the OTMs at the required temperature for operation as well. Thus, the O_2 separation system is thermally and chemically integrated with the combustion system. Based on the economic analysis conducted to date, a boiler with integrated ceramic membranes has the potential for substantial capital and operating cost savings when CO_2 capture is required. In the case of a more conventional boiler without CO_2 capture, the energy savings can potentially pay for the incremental cost of the OTM boiler in ~ 2 years.

INTRODUCTION

The capture of CO_2 from combustion sources can be accomplished by a variety of techniques, including adsorption, membrane separation, low-temperature distillation, absorption, and compression. The low partial pressure of CO_2 (less than 10%) in the exhaust of conventional air-fired boilers makes diffusion and temperature-driven separation techniques difficult and expensive. However, by increasing the partial pressure of CO_2 and decreasing that of diluents (N_2, O_2, etc.), the carbon dioxide may be easily separated using a series of compressors and heat exchangers at a reduced cost compared to alternative methods.

One effective approach to produce a CO_2-rich flue gas from a combustion process is to use pure oxygen rather than air as the oxidant stream. Oxy-fuel fired combustion systems offer a number of advantages over air-fired systems. Over the last three decades, oxy-fuel fired processes have demonstrated: (i) increased fuel efficiency, (ii) reduced pollutant emissions (e.g., NO_x), and (iii) improved productivity/throughput [1]. These advantages coupled with the fact that the exhaust products contain a high concentration of CO_2 make oxy-fuel fired systems ideal candidates for high-efficiency boilers with CO_2 sequestration. As with any technology, the performance advantages must justify the associated costs. To date, the primary issue limiting the application of oxy-fuel fired systems to a larger market is the cost of producing oxygen (i.e., separating O_2 from other gases present in air). Modern systems that exhibit high-thermal efficiencies have typically not been candidates for oxy-fuel conversion because the incremental improvements in thermal efficiency are typically not sufficient to offset the cost of oxygen production.

One technology that is expected to significantly reduce the cost of oxygen production utilizes oxygen transport membranes (OTMs), which selectively transport O_2 across a ceramic membrane. The driving force for transport is a concentration gradient across the membrane. Past work has identified a target operating temperature of the membranes of approximately 800–1100 °C (1500–1800 °F). In low temperature processes or standalone systems, the energy required to maintain this operating temperature must be supplied by an external source. However, in high-temperature systems, the integration of the OTM components with a heat-generation system such as a boiler, can offer many advantages. Combustion systems, in particular boilers, are ideal candidates for this integration. First, the flux of O_2 through the OTM material is driven by the gradient of the O_2 partial pressure across the membrane. By supporting the combustion process on the surface of the OTM tube, a sink for O_2 is created on the permeate side of the tube, thereby allowing significant O_2 fluxes to be achieved. Additionally, heat generated by the combustion supplies the energy required to activate the OTM materials, and the desired operating temperature is maintained by locating steam tubes near the OTM surfaces. Thus, the implementation of OTM technology into a boiler represents a method that will allow the benefits of oxy-fuel combustion to be extended to fire processes that have not been suitable candidates to date. More importantly, this will facilitate the integration of CO_2 sequestration in a technically compelling and economically competitive manner. Figure 1a and b illustrate the basic configuration of an OTM boiler system with CO_2 capture and a conventional air-fired system with CO_2 capture. Because of the low concentration of CO_2 in the exhaust of the air-fired system, a chemical absorption process is required to remove the CO_2, thus adding to the cost and complexity of the system.

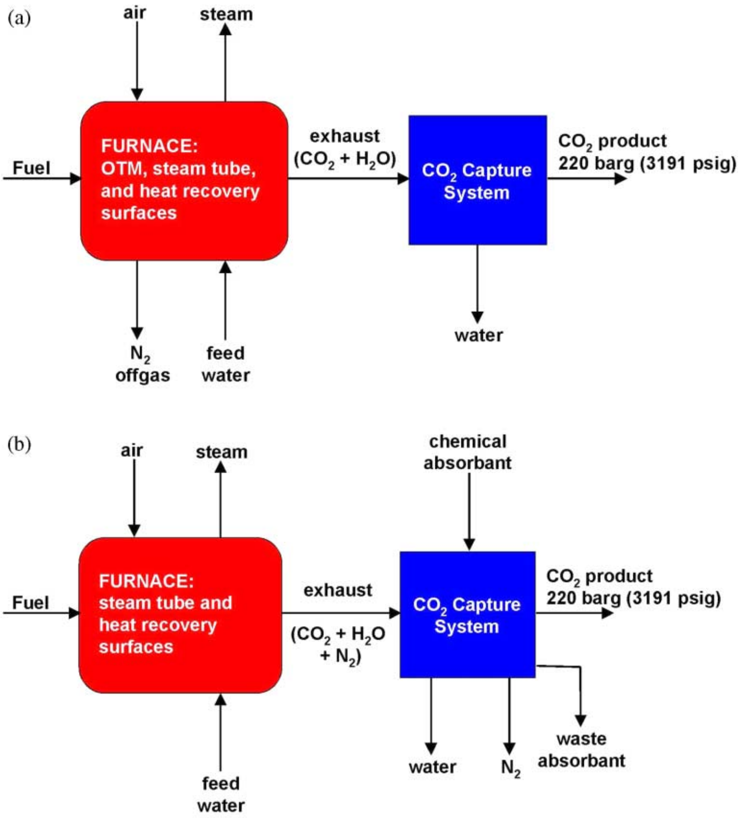

Figure 1: Conceptual layout of a boiler system with CO_2 capture using (a) oxy-fuel combustion via OTM surfaces and (b) an air-fired conventional boiler system with chemical capture of CO_2.

This chapter focuses on a refinery scenario, which involves the development of a design and cost estimate for a boiler that uses OTM technology to replace a specified air-fired boiler system used in a refinery. The OTM boiler is to be based on the advanced boiler concept under development by Praxair, Inc. The advanced boiler is an oxy-fuel fired boiler in which the oxygen is supplied by OTM surfaces integrated with the boiler system. The system must also sequester the CO_2 from the boiler exhaust and purify it to the desired specifications. The remainder of the introduction establishes further background information on OTM systems and CO_2 capture. The study methodology section contains the advanced boiler system design and explanation of the models used to size the system. The results and discussion section illustrates the size, operating parameters and cost of the system.

Background

Oxygen transport membranes

Ceramic membranes offer a method for substantially reducing the cost of oxygen production in the future. The characteristic that makes ceramic membranes attractive is their virtually infinite selectivity for oxygen. This only occurs at temperatures above ~600 °C (1100 °F). There are two basic types of ceramic membranes, electrically driven and pressure driven. In the case of the electrically driven membranes, only oxygen ions can pass through the membrane, and an external circuit and electric power source are required to transport electrons. Pressure-driven membranes have a higher partial pressure of oxygen on the retentate side of the membrane than on the permeate side. The partial pressure difference of oxygen across the membrane provides the driving force for the separation. These membranes are called *mixed conducting* because they allow oxygen ions to flow in one direction and electrons to flow back in the other, thus completing the internal electric circuit. In order for the process to occur, the oxygen molecule must first be adsorbed on the surface, dissociated, and converted to an oxygen ion, as illustrated in Figure 2. The higher partial pressure on the retentate side versus the permeate side provides the driving force to enable the oxygen ion to pass through the membrane. On the permeate side of the membrane, the oxygen ions recombine to form oxygen molecules and release the electrons to flow back through the membrane. The higher partial pressure can either be created by high-pressure air on the retentate side of the membrane and low-pressure oxygen on the permeate side of the membrane or by consuming the O_2 (i.e., via chemical reaction) on the permeate side of the membrane. The resulting low oxygen concentration due to the ongoing chemical reaction maintains the driving force across the membrane. When this is the case, low-pressure air can be supplied on the retentate side of the membrane, and the permeate side can be at a similar or even greater absolute pressure. By consuming O_2 via combustion the energy required for oxygen separation is minimized, thus making oxy-fuel combustion economically viable. These ceramic membranes are sometimes called OTMs, ion transport membranes (ITMs), mixed ionic-electronic conductors (MIEC) or solid electrolyte conductors (SELIC).

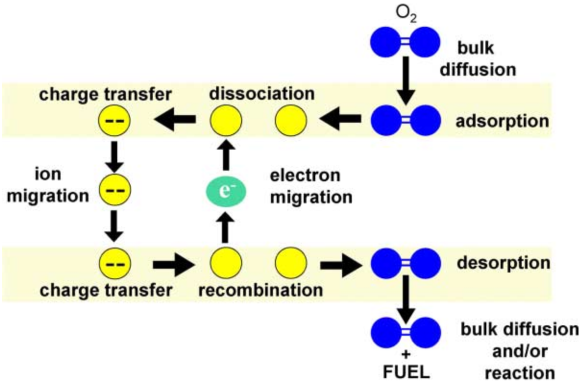

Figure 2: Process of oxygen transport through a ceramic membrane.

Numerous potential applications for these types of transport membranes are currently being investigated. Some applications include oxygen purification for integrated gasification combined cycle (IGCC) power plants, oxy-fuel fired boilers with integrated ceramic membranes and CO_2 sequestration, and incorporation in partial oxidation reactors for syngas production.

The two main areas of development needed for a successful OTM-containing boiler are the ceramic membrane materials and the thermal management. Key objectives include the following:

- Reliable ceramic elements need to be developed that have adequate flux, strength and suitable mechanical and thermal stability at temperature.
- The elements need to be manufactured cost-effectively and defect free.
- Suitable processes need to be developed and tested to demonstrate temperature control, heat transfer and energy efficiency.

A facility capable of manufacturing ceramic elements for beta site boilers has been constructed, and is currently being operated to produce OTM surfaces for experimentation.

Perovskite-related materials (ABO_3, where A and B are transition elements) have been the most tested materials to this point. These materials have been subjected to multiple thermal and pressure cycles. For one such material, the concentrations of CO_2, O_2, and N_2 are plotted versus run time in Figure 3a under a single set of experimental conditions. The contamination-free fuel is completely combusted when a ceramic OTM surface supplies pure oxygen. Over 16,000 h of testing have been conducted under these conditions with membrane temperatures in the range 1000 °C (1800 °F). The goal of the current program is to design, manufacture, and quality assure ceramic elements to have an operating life greater than 10 years in continuous service. Figure 3b is a plot of the log of the creep versus decreasing temperature, in which the target operating temperature is represented by “TT”. The data demonstrate the improvements that have been made to OTM materials in terms of strength characteristics.

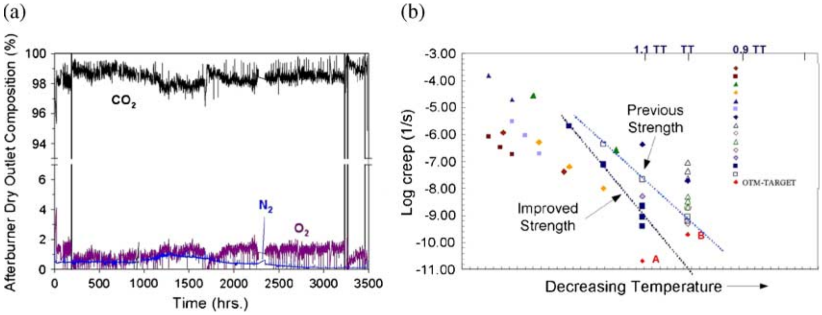

Figure 3: (a) Composition of exhaust in a system using contamination-free fuel and OTM surfaces to supply oxygen during a 3500 h test run, and (b) log of creep versus decreasing temperature for a variety of OTM test materials.

CO_2 capture

The most viable techniques for the recovery of CO_2 from the exhaust gas of an oxy-fuel fired system are chemical absorption and flue gas compression. Praxair, Inc. has extensive experience in both amine-based CO_2 capture systems and the design of compression systems for gases. Potential designs and costs have been explored for a variety of CO_2 separation systems. Absorption systems are generally required for air-based combustion flue gases where CO_2 concentrations are low, while oxy-fuel fired systems have the option of compressing the flue gas to recover CO_2.

STUDY METHODOLOGY

Advanced Boiler System Design

The overall design of the advanced boiler and CO_2 capture system consists of three basics parts: a furnace section, a heat recovery system, and an exhaust compression system. This concept is illustrated schematically in Figure 4. The furnace section combusts the fuel and produces steam as a product. This part of the unit contains the ceramic membranes and steam tubes. A portion of the unused heat from the furnace section is recuperated in the heat recovery system. In this section, the hot exhaust and N_2-rich OTM offgas from the furnace section are utilized to preheat the incoming air and feed water streams. Finally, in the exhaust compression system, a series of compressors and heat exchangers are used to remove the water from the exhaust and compress the remaining CO_2 into a supercritical product. The specifications for the boiler and CO_2 product stream are presented in Table 1. Note that the boiler feedwater and inlet air are supplied to the system at an elevated temperature (relative to ambient) due to the assumption of heat recovery using these streams in another part of the facility containing the boiler.

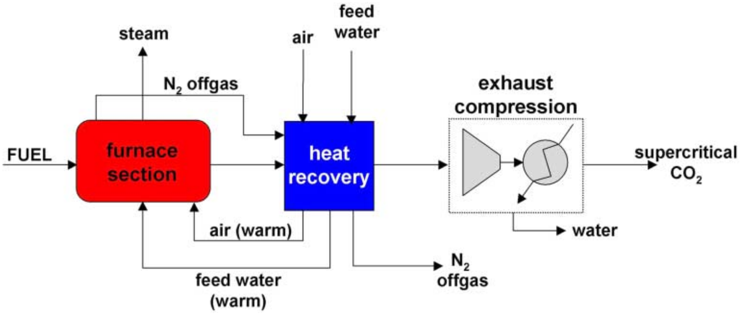

Figure 4: Overall layout of the advanced boiler with CO_2 capture.

TABLE 1
BOILER AND CO_2 SPECIFICATIONS

Variable	SI units	US units
Boiler Specs.		
Delivered steam	63 kg/s	500,000 lb/h
Steam conditions — pressure	128 barg	1856 psig
Steam conditions — temperature	518 °C	964 °F
Feedwater temperature	149 °C	300 °F
Inlet air temperature	74 °C	165 °F
CO_2 Specs.		
Pressure	220 barg	3191 psig
Purity (molar dry basis)	97%	97%
Inerts (N_2 + Ar, molar basis)	3%	3%
NO_x, SO_x, CO, HC, O_2	Unrestricted	Unrestricted
Water (max.)	50 ppm	50 ppm
Temperature (max.)	50 °C	122 °F

Furnace layout and modeling

Selection of furnace design. In order to separate oxygen from air by utilizing pressure-driven OTMs, the membranes must be hot (800–1100 °C (1500–2000 °F)) and an O_2 concentration gradient must be established across the membrane. This is done by removing O_2 molecules from the permeate side of the membrane. Two possible methods to remove O_2 molecules from the surface of a pressure-driven OTMs are *gas purge* and *reactive purge* [2]. The reactive purge method (Figure 5a) uses a chemical reaction of the O_2 molecules with a fuel to remove the O_2 from the OTM surface. Since the O_2 reacts almost instantly on the permeate side of the membrane, the partial pressure of O_2 on the retentate side (P'_{O2}) is several orders of magnitude higher than the O_2 partial pressure on the permeate side (P''_{O2}) of the membrane. Thus, there is a substantial driving force to transport O_2 through the membrane. In the gas purge method (Figure 5b), a gas (e.g., recirculated flue gas) is swept over the surface of OTM in order to transport the O_2 molecules away from the surface. The partial pressure of O_2 on the retentate side is only slightly larger than that on the permeate side, and the flux of O_2 through the membrane is not nearly as large as in the reactive purge case.

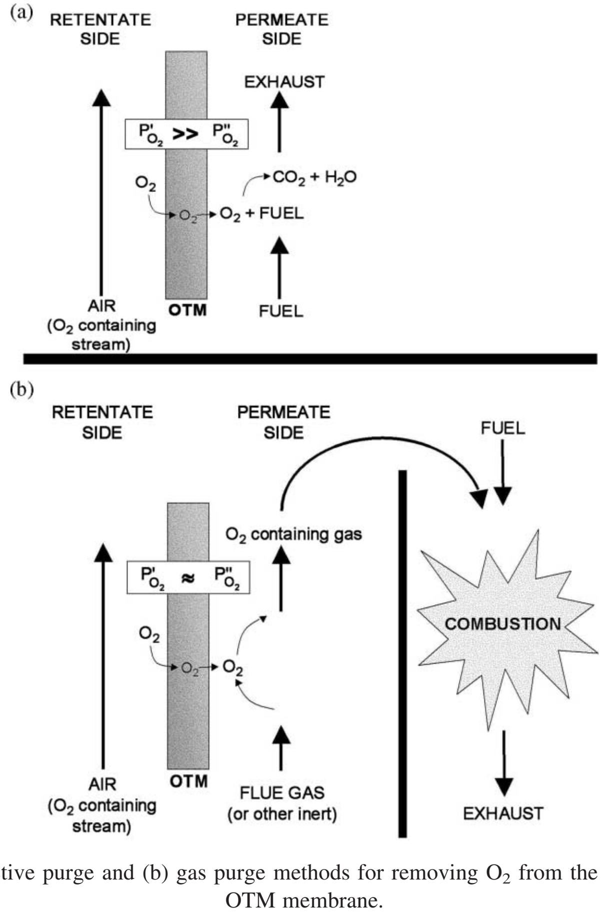

Figure 5: (a) Reactive purge and (b) gas purge methods for removing O_2 from the permeate side of an OTM membrane.

Three basic designs for the advanced boiler model have been considered. In the first design, tubes with OTM membranes are placed in a parallel configuration with steam tubes, and the oxygen source (air) flows on the inside of the tubes (Figure 6a). External to the OTM tubes, fuel and recirculated flue gas flow parallel to the tubes in either a counter- or co-flow pattern, thus utilizing reactive purge to maintain the O_2 flux [3]. The main advantages of this method are the compact size and the complete thermal integration of the air separation process. The main disadvantages of the co/counter-flow design are membrane mechanical instabilities due to the temperature gradients down the length of the OTM tubes and the harsh furnace environment. These factors could result in a decrease of OTM lifetime of up to 50%. Also, the pressure drop through the furnace would be large due to the tight tube pattern in the system.

The second design considered uses an external air separation unit with OTM surfaces to supply O_2 to the boiler [4]. Figure 6b illustrates the concept. High-pressure air from a compressor is fed through a series of heat exchanging tubes inside the furnace to preheat the air, which is then brought to the OTM unit located outside of the furnace. The permeate of the OTM unit (pure O_2) is then inserted back into the furnace with the fuel through oxy-fuel burners. The advantages of this method include the ability to retrofit an existing boiler and the fact that the OTMs would not be in contact with the harsh furnace environment. The major disadvantage is the high capital cost of the compressor equipment that supplies the feed air. This design would have neither gas purge or reactive purge, thus a large pressure differential would need to be established across the membranes to create the desired O_2 flux.

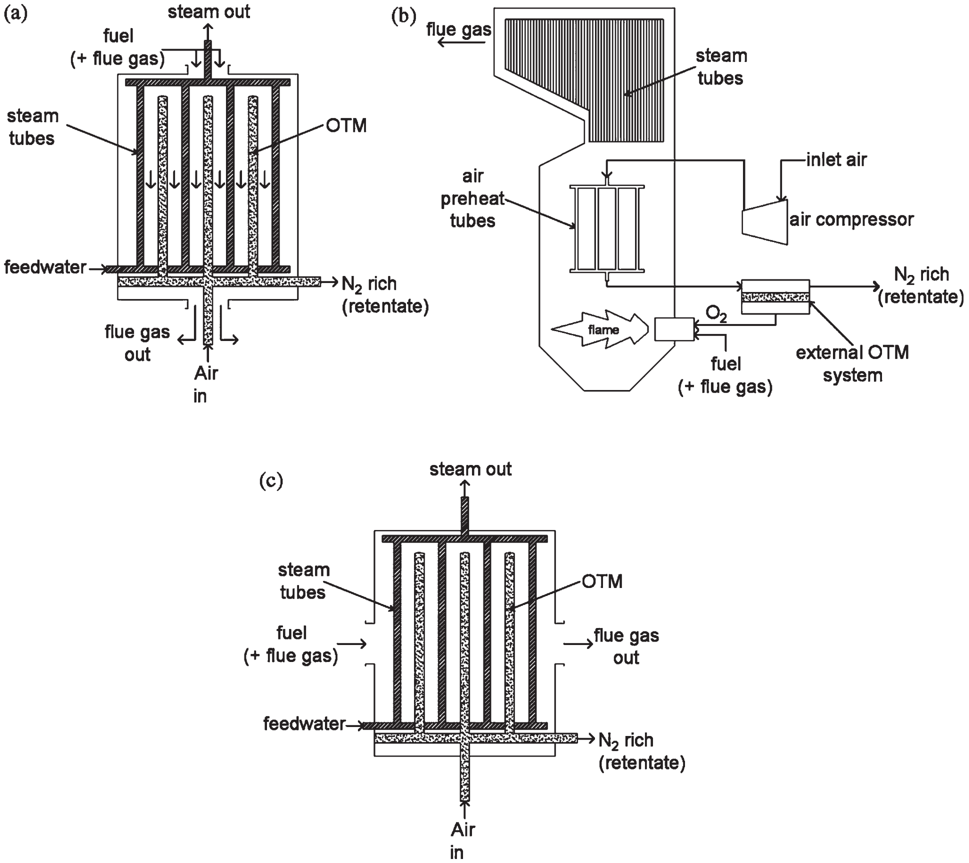

Figure 6: The advanced boiler designs investigated were the (a) co/counter-flow design, (b) external membrane design, and the (c) cross-flow design.

The third design considered thermally integrates the OTM tube surfaces in the furnace in a similar manner as the co/counter-flow design, but the tubes are positioned perpendicular to the exhaust flow direction [5]. This design is known as the cross-flow advanced boiler furnace, and the concept is represented in Figure 6c. The system could be built using either a gas purge method or the reactive purge method. The reactive purge design was chosen because the flux of O_2 is higher in such a system, and the amount of flue gas that must be recirculated is reduced. The advantage of this design over other thermally integrated designs is that the OTM tube temperature remains relatively constant along the tube length. Also, the pressure drop through the furnace is not as severe as the co/counter-flow design. The system disadvantages still include potentially shortened OTM lifetimes in the harsh furnace environment and poor turndown capabilities, but the relative simplicity of this furnace design makes it more likely to succeed.

Furnace section layout

The furnace section of the advanced boiler produces steam from a feed water supply by combusting a gaseous fuel with pure O_2 supplied via OTM tubes. The furnace section is divided into two sections, one that produces saturated steam and another that superheats the steam to the desired specifications. The ceramic membrane surfaces are structured on tubes that are placed along the length of the furnace, perpendicular to the direction of exhaust gas flow. Steam tubes are placed parallel to the OTM tubes along the furnace. The number of steam tubes is dictated by the amount of heat removed to maintain the OTM surfaces at a specified operating temperature. Figure 7 illustrates the proposed design for the furnace section.

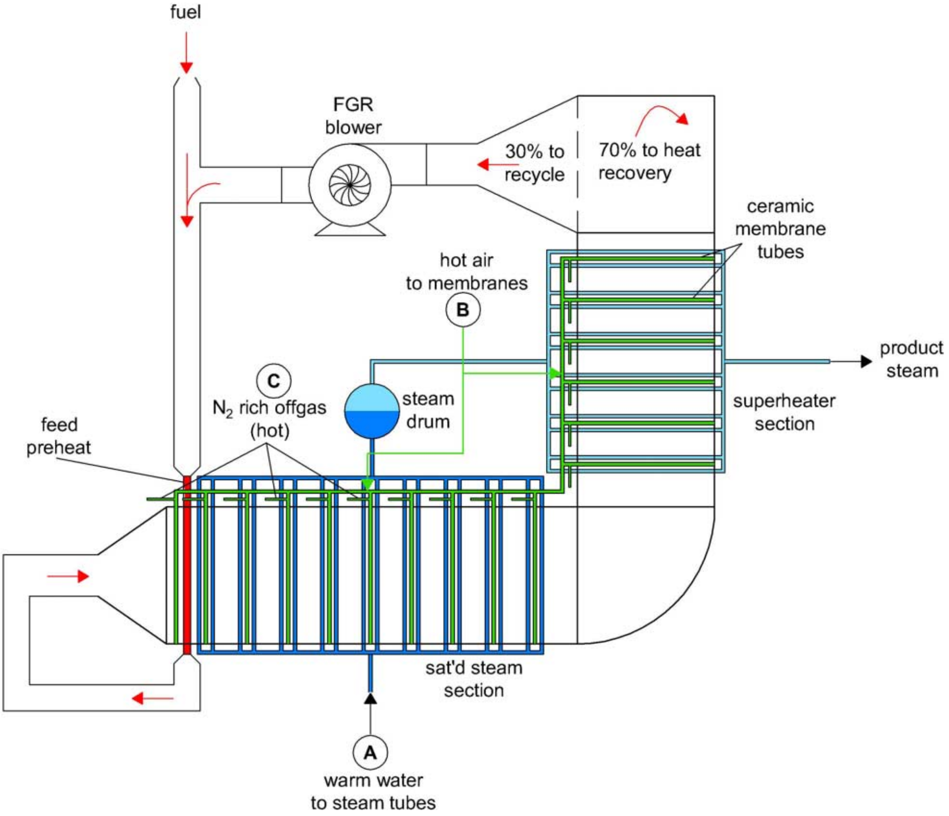

Figure 7: Furnace section layout.

Fuel is injected into the system and mixed with a portion of the recycled flue gas. This dilute fuel mixture is then passed through heat transfer tubes in the front end of the furnace in which the mixture is preheated and injected into the furnace. The fuel mixture contacts O_2 on the surface of the OTMs and is combusted. The OTM tubes are arranged perpendicular to the flow direction. The furnace model used throughout this report assumes that the combustion takes place on or very near the tube surface. Previous modeling and experimental work suggests that combustion occurs on the surface of the membrane. The fuel and exhaust products pass over the various rows of OTM tubes and steam tubes to the end of the furnace section of the boiler. At this point, a portion of the exhaust is withdrawn to be mixed with the incoming fuel, and the remaining material moves on to the heat recovery section of the boiler.

Steam tubes are placed parallel to the OTM tubes. The number of steam tubes varies in any particular row of tubes. This is to ensure that the correct quantity of heat is withdrawn to maintain a constant temperature on the tube surfaces. The first two-thirds of the furnace section is devoted to supplying saturated steam to a steam drum, and the exhaust flow horizontally. The exhaust–fuel mixture then flows vertically through the remaining part of the furnace section, which superheats the steam.

Hot air from the heat recovery system is fed to the OTMs in order to supply O_2 for combustion. The hot air enters the OTM manifold and is evenly distributed amongst all of the OTM tubes in the furnace. The hot nitrogen-rich offgas from the OTMs exits each tube and is combined back into a single flow before moving on to the heat recovery section. This N_2-rich stream may be further processed to produce an N_2 product if desired.

The fuel used in this study was natural gas with the composition listed in Table 2. Other fuel gases, such as refinery gas fuels, may be utilized if the sulfur content is low ($H_2S < 0.5$ ppm). Emissions from the boiler in the form of NO_x will depend on the operating temperature and the amount of N_2 present during combustion. The only sources of N_2 are from natural gas and any leakage of air into the system. However, the furnace will be operated at a relatively low temperature, thus NO_x production should be quite limited.

TABLE 2
NATURAL GAS COMPOSITION

Species	**Mol%**
Methane	94.4
Ethane	3.0
Propane	0.5
Butanes	0.2
Pentanes	0.1
Hexanes +	0.1
Nitrogen	1.5
Carbon dioxide	0.2

Specific Gravity, 0.589; LHV, 34.82 MJ/sm^3 (934 BTU/scf), “standard” conditions (1.013 bar, 15.5 °C (14.7 psia atm, 60 °F)); HHV 38.62 MJ/sm^3 (1037) BTU/scf) “standard” conditions (1.013 bar, 15.5 °C (14.7 psia atm, 60 °F)).

Furnace section modeling. A global network model was developed to evaluate furnace performance and estimate the size requirements. The furnace was divided up into N stages in which each stage contains a row of OTM tubes and an unknown number of steam tubes. A material and energy balance was solved on each section in order to calculate the unknown quantities. The model is illustrated schematically in Figure 8. In the model, F_i is the molar flow rate of fuel, products of combustion and residual oxygen in the flue gas into stage i, W_i is the molar flow rate of the nitrogen-rich offgas stream leaving the OTM tubes of stage i, Q_i is the heat transferred to the water/steam in stage i, and R is the recycle ratio. In each stage, the F streams and W streams have no direct contact except via mass transfer of O_2 across the membranes.

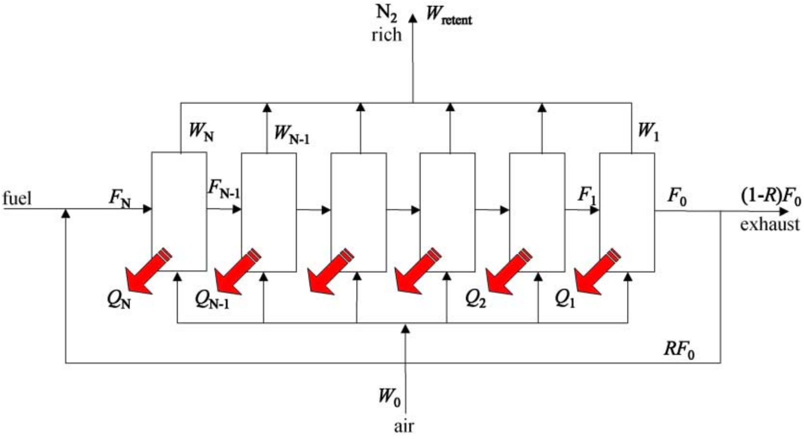

Figure 8: Schematic representation of the furnace section model.

In order to simplify the calculations, a number of assumptions were made:

- constant O_2 flux in each stage;
- no external heat losses;
- complete combustion in each stage (O_2 is completely consumed);
- tube wall temperatures same as that of inner fluid;
- recycle ratio of 30–40% ($R = 0.3–0.4$);
- excess O_2 in exhaust of 1%;
- no air leakage into combustion environment.

Thus by knowing the inlet and outlet conditions of the furnace, OTM surface temperatures, OTM tube sizes, and O_2 flux, the flow rates, compositions, gas temperatures, and heat removal with steam (Q_i) are calculated at each stage by solving the material and energy balances simultaneously.

Heat recovery system
The hot exhaust gas and the hot N_2-rich offgas from the OTM tubes are sent to the heat recovery system to recuperate some of the sensible and latent heat by preheating the inlet air and feed water. Figure 9 illustrates a layout for this system.

Upon leaving the furnace section of the boiler, the hot exhaust gas changes direction and flows downward over the heat exchangers. First, the exhaust gas passes over the inline economizer to preheat the feed water. The partially cooled exhaust then passes over an air preheater, in which some of the water is condensed out of the gas and collected. The remaining exhaust passes through the system induction blower and to the exhaust compression system. The N_2-rich offgas passes through two external heat exchangers. The first exchanger further preheats the incoming air to a temperature within approximately 100 °C (180 °F) of the operating temperature of the OTM tubes. The second exchanger supplies additional heat to the feed water and reduces the N_2-rich offgas temperature to the final conditions. Because of the high inlet air and water temperatures specified in this test case (see Table 1), the energy efficiencies are lower than they would be with ambient temperature air and water feeds. The cooling load on the CO_2 system would also be reduced in the case of ambient feed streams.

The heat recovery system was modeled using HYSYS 3.0.1 [6] with inputs from the furnace model. First, the temperatures for the inlet flows were assumed in the furnace model, and the exhaust gas and N_2-rich offgas conditions were calculated. The results were inserted into the HYSYS model and the new inlet

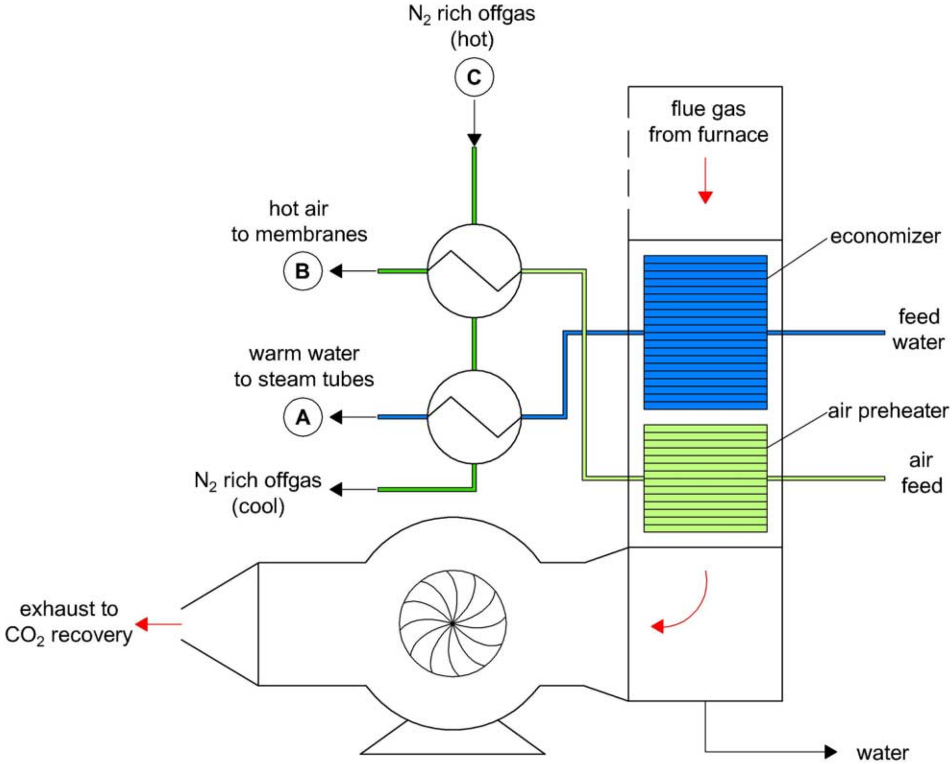

Figure 9: Heat recovery system layout.

temperatures were calculated for the furnace section. This method was repeated until the temperature of the inlet materials converged to within the desired tolerances.

Exhaust compression system
The cooled exhaust stream from the heat recovery system is fed to the exhaust compression system in order to recover the CO_2 as a supercritical fluid. The exhaust gas passes through a cooler to remove more of the water vapor. It then goes through a series of two centrifugal screw compressors and coolers. The remaining water is removed in a dryer. The dry CO_2 gas then goes through two reciprocating compressors with after-coolers to compress it into a supercritical fluid. The flow diagram for this process is shown in Figure 10. The compression of the exhaust gas was modeled using HYSYS 3.0.1.

RESULTS AND DISCUSSION

Operating Conditions of the Advanced Boiler

A series of design conditions were specified in order to size a system to achieve the steam output stipulated in the refinery scenario (see Table 1). A list of values assumed for the design criteria appear in Table 3.

The values mentioned above were used in the model developed for the advanced boiler in order to produce a boiler design. This includes the boiler size, number of ceramic tubes, number of steam tubes, heat exchanger areas, compressor loads, blower loads, and stream conditions (i.e., temperature, pressure, composition).

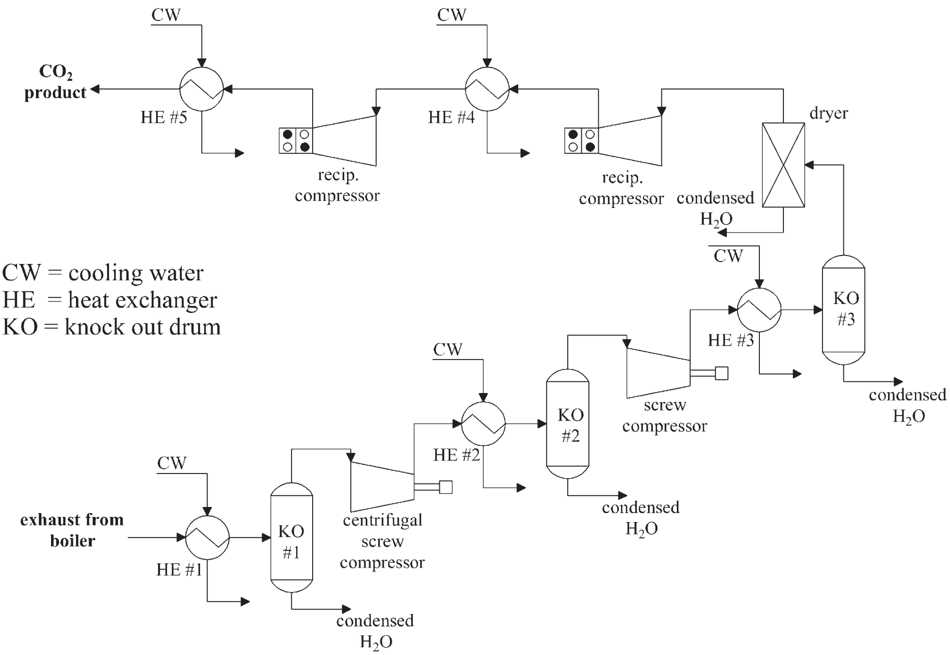

Figure 10: Flow diagram of the exhaust compression system.

TABLE 3
DESIGN CONDITIONS FOR THE ADVANCED BOILER

Variable	SI units	US units
OTM tube diameter (outer)[a]		
OTM tube diameter (inner)[a]		
OTM tube length[a]		
Number of tubes/row[a]		
OTM operating temperature	800 °C	1472 °F
Steam rate	63 kg/s	500,000 lb/h
Feed water temperature	149 °C	300 °F
Steam temperature	518 °C	964 °F
Delivered steam pressure	129 bar	1871 psia
Steam tube diameter (outer)	0.0381 m	1.5 in.
Feed air temperature	74 °C	165 °F
O_2 mole fraction in air	0.209	0.209
O_2 mole fraction in N_2-rich retentate	0.05	0.05
O_2 mole fraction exhaust	0.01	0.01
Fuel temperature	25 °C	77 °F

[a] Value omitted due to confidentiality.

Table 4 summarizes the design parameters calculated for the advanced boiler using the model described in the study methodology section.

TABLE 4
CALCULATED PARAMETERS FOR THE ADVANCED BOILER DESIGN

Variable	SI units	US units
Furnace dimensions		
Furnace chamber width	6.1 m	20 ft
Furnace chamber height	3.05 m	10 ft
Furnace chamber linear length	18.3 m	60 ft
Footprint	150 m^2	1600 ft^2
Number of rows of tubes	25	25
Total linear length of OTMs[a]		
Total linear length of steam tubes[a]		
Flow rates		
Natural gas mass flow rate	700 kmol/h	1560 lbmol/h
Natural gas volume flow rate (std.)	5.0 sm^3/s	638,000 scfh
Air flow rate	9100 kmol/h	19,900 lbmol/h
O_2 flow per row of OTMs	68 kmol/h	150 lbmol/hr
N_2-rich offgas out	7600 kmol/h	16,700 lbmol/h
Exhaust flow out (before FGR)	2350 kmol/h	5200 lbmol/h
Recycle ratio (%)	30	30
Temperatures		
Average furnace temperature	850 °C	1560 °F
Preheated air (after heat rec. sys.)	800 °C	1470 °F
Feedwater (after heat rec. sys.)	220 °C	425 °F
N_2 offgas (cool)	207 °C	405 °F
Exhaust (feed to CO_2 capture)	75 °C	167 °F
Blower parameters		
Recycle blower power	33 kW	1.1×10^5 BTU/h
Main exhaust blower power	376 kW	1.3×10^6 BTU/h
Air supply blower	4000 kW	1.4×10^7 BTU/h

[a] Value omitted due to confidentiality.

Operating Conditions of the CO_2 Capture System

The CO_2 capture system consists of a series of heat exchangers and compressors (Figure 10) that completely removes the water from the exhaust and compresses the product into a supercritical fluid for storage. Table 5 lists the required duties and flow conditions of the CO_2 capture system.

Conventional Boiler Design

A modern conventional boiler system would have similarities to the advanced boiler such as a furnace section, heat recovery section, and CO_2 capture system. However, each of these subsystems would have substantially different components. The conventional boiler simply blows warm air into the furnace with the fuel and combustion occurs in the presence of a large amount of N_2. The heat recovery system would be made up of only a feed water economizer and air preheater. Finally, a chemical absorption system would need to be used to capture the CO_2 out of the exhaust stream, because of the relatively low concentration of CO_2.

TABLE 5
CO_2 CAPTURE SYSTEM FLOW RATES AND DUTIES

Variable	**SI units**	**US units**
Flow rates		
Exhaust gas feed	1260 kmol/h	2800 lbmol/h
Exhaust gas composition: (after furnace and partial H_2O removal)		
CO_2	0.606	0.606
H_2O	0.376	0.376
O_2	0.018	0.018
CO_2 out	9.1 kg/s	71,900 lb/h
CO_2 purity (%)	97	97
Temperature and pressure		
Feed temperature	75 °C	167 °F
CO_2 product temperature	115 °C	239 °F
CO_2 product pressure (absolute)	221 bar	3200 psia
Duties		
Cooling water	314 kg/s	2,490,000 lb/h
Compressor power	4200 kW	1.4×10^7 BTU/h
Dryer power	3 kW	1.2×10^4 BTU/h

The material and energy balances for an air-fired boiler are summarized in Table 6. These calculations represent only the boiler and heat recovery (no CO_2 capture). Steam production, air feed temperature, and feed water temperature are the same as those listed above for the advanced boiler.

TABLE 6
CONVENTIONAL BOILER VALUES

Variable	**SI units**	**US units**
Fuel feed (natural gas)	760 kmol/h	1700 lbmol/h
Air feed	9200 kmol/h	20,300 lbmol/h
Exhaust gas	10,100 kmol/h	22,200 lbmol/h
Exhaust gas composition: (after furnace and partial H_2O removal, mole fraction)		
CO_2	0.08	0.08
H_2O	0.16	0.16
O_2	0.03	0.03
N_2	0.73	0.73
Exhaust temperature	100 °C	212 °F
Duty on exhaust blower	75 kW	2.6×10^5 BTU/h
Duty on air inlet blower	70 kW	2.4×10^5 BTU/h
Furnace dimensions		
Width	15.2 m	50 ft
Depth	7.6 m	25 ft
Height	9.8 m	32 ft

Costing and Energy

Equipment costs

Based on the design proposed in the Section "Operating Conditions of the Advanced Boiler", and expected ceramic membrane manufacturing costs, an advanced boiler using OTM technology is expected to cost approximately \$8.5 million. This is an installed cost estimate on an US gulf coast basis. It includes all of the heat exchangers, fans and controls.

The major cost components of the CO_2 capture system are the compressors. The complete installed capital cost estimate for the CO_2 capture system is estimated at US\$6 million. The basic breakdown of the CO_2 system costs is illustrated in Table 7.

TABLE 7
CO_2 CAPTURE SYSTEM COSTS FOR AN OTM-BASED BOILER

Equipment grouping	**Installed cost**[a]
Screw compressors	\$2,000,000
Reciprocating compressors	\$2,000,000
Heat exchange equipment	\$1,300,000
Drying equipment	\$700,000
Total	\$6,000,000

[a] US Gulf Coast basis.

The capital cost of a conventional air-fired boiler is approximately US\$6 million. This assumes a field-erected unit that produces 63 kg/s (500,000 lb/h) of steam at the specified conditions. This unit would also be capable of firing fuel oil as a back-up source of energy. As a point of comparison with the advanced boiler, a cost estimate was made for a system to remove the CO_2 from the exhaust stream of this conventional boiler. The system is based on technology (Praxair, Inc.) that uses amine absorption. The capital expenditure for such a system is estimated to be approximately US\$30 million, or more than five times the cost of the advanced boiler CO_2 capture system. The breakdown of the costs for a CO_2 capture system for the air-fired boiler described above appears in Table 8.

TABLE 8
CO_2 CAPTURE SYSTEM COSTS FOR AN AIR-FIRED BOILER

Equipment grouping	**Costs**[a]
Pretreatment	\$2,560,000
Absorber	\$2,560,000
Regeneration section	\$3,800,000
Heat exchange equipment	\$1,280,000
Compression equipment	\$2,700,000
Other (controls, construct.)	\$2,600,000
Engineering and construction	\$15,000,000
Total	\$30,500,000

[a] US Gulf Coast basis.

Energy requirements

The advanced boiler has some distinct advantages over a conventional air-fired boiler in terms of fuel savings. However, additional power is needed for the CO_2 system and the feed air blower. The feed air blower must supply air to the OTM manifold and maintain the air flow through this complex system of tubes. The compression ratio required for the feed air blower or compressor is approximately 1.25–1.5. Another major source of energy requirements for the advanced boiler is the cooling water in the CO_2 capture system. Table 9 summarizes the energy requirements of the two systems.

TABLE 9
ENERGY REQUIREMENTS FOR THE ADVANCED BOILER AND CONVENTIONAL BOILER

Variable	**SI units**	**US units**
Advanced boiler		
Fuel input (HHV)	188 MW	642 MMBTU/h
Power to furnace blowers	4.4 MW	15 MMBTU/h
Power to CO_2 compressors	4.2 MW	14 MMBTU/h
Cooling water	0.314 m^3/s	5000 gpm
Conventional boiler		
Fuel input (HHV)	201 MW	685 MMBTU/h
Power to furnace blowers	0.15 MW	0.5 MMBTU/h

From the values stated in Table 9, it is apparent that the advanced boiler offers an energy cost savings over the conventional boiler, even with the CO_2 capture system included. Approximately 13 MW (43 MMBTU/h) less fuel is required in the advanced boiler relative to the conventional air-fired boiler sized for this case. The pressure drop across the OTM manifold requires a large compressor or blower to feed air to the advanced boiler. This blower requires about 4 MW (14 MMBTU/hr) of additional energy. The addition of the CO_2 capture system requires another 4.2 MW (14 MMBTU/h) of energy and 0.3 m^3/s (5000 gpm) of cooling water. Thus, the advanced boiler with CO_2 capture still shows an advantage in energy efficiency over the conventional boiler.

Cost comparison

Table 10 illustrates a cost comparison between a conventional boiler with CO_2 capture system and a comparable OTM-based system. The advanced boiler alone costs ~40% more than a conventional boiler of equivalent size. However, when the CO_2 capture system is added, the capital cost is ~60% less. The current advanced boiler configuration results in a fuel savings of about 6% over the conventional system. Again, when the energy requirements associated with CO_2 capture are added in, the OTM system offers a substantial overall energy savings. As shown in Table 10, the CO_2 capture energy required for the advanced boiler is over 80% less than the energy required for an amine-based system on a conventional boiler. Figure 1 and Table 1 define the scope and specifications for the systems.

The economics of CO_2 capture is commonly expressed in terms of \$/ton of CO_2 avoided. This quantity was calculated for both the advanced boiler and a conventional boiler in which the CO_2 capture system was added. The capital cost basis is relative to a \$6,000,000 conventional boiler investment. Assuming a 15-year lifetime and 12% rate of return, the cost to remove CO_2 using the advanced boiler with exhaust compression on an annual basis is approximately \$9.30/ton of CO_2 avoided. Using a condensing heat exchanger gives an operating cost savings that leads of a CO_2 removal cost of \$5.30/ton CO_2 avoided. Alternatively, by adding a CO_2 capture system to a conventional boiler, the recovery cost of about \$42/ton CO_2 is avoided.

TABLE 10
COST COMPARISON OF BOILER OPTIONS FOR SYSTEM COSTS AND CO_2 CAPTURE ENERGY

Costs[a]	**Conventional boiler**	**Advanced OTM boiler**
System costs		
Boiler	\$6,000,000	\$8,500,000
CO_2 capture system	\$30,500,000	\$6,000,000
Total capital	\$36,500,000	\$14,500,000
% Savings		60%
Annual fuel cost at \$3.5/MMBTU (\$0.0033/MJ)	\$21,000,000	\$19,700,000
Annual power cost at \$0.045/kWh	\$52,600	\$1,500,000
Total boiler operating cost	\$21,100,000	\$21,200,000
Operating cost savings with condensing heat exchanger		\$1,300,000
CO_2 capture energy		
Annual steam at \$3.5/MMBTU (\$0.0033/MJ)	\$4,100,000	
Annual power at \$0.045/kWh	\$2,900,000	\$1,500,000
Annual chemicals	\$1,500,000	
Annual totals	\$8,500,000	1,500,000
% Savings		83%

[a] US Gulf Coast basis.

Technological and Cost Uncertainties

A number of assumptions have been made in calculating the design variables of the advanced boiler and CO_2 capture system. Thus, some uncertainties exist is this design and the associated cost structure. Some of these potential unknowns are now addressed.

The design of the Advanced Boiler furnace uses OTM tubes for the air separation process. The assumption of a constant O_2 flux at each stage of the furnace implies that tubes of with varying composition must be used down the length of the furnace. A major cost and technical uncertainty is the ability to manufacture robust OTMs with varying performance criteria. Fabrication processes for commercial manufacturing of robust ceramic tubes are currently under development.

Since the fuel needs to enter the combustion chamber at an elevated temperature and a fuel-rich environment is present, the possibility exists for coke formation. Coking can result in clogging of the OTM surfaces thereby limiting O_2 transfer. Thus, the optimum exhaust recycle ratio must be established, the optimum temperature at which the fuel gas enters the furnace, and the optimum location of fuel insertion (fuel staging). It is not well understood where combustion takes place once the fuel comes in contact with the OTM environment. Future research should help with the understanding of integrated combustion/OTM systems. An improved understanding of the reactions that take place within integrated systems will allow optimization of the gas path and in furnace heat transfer.

The assumptions of no external heat losses and an assumed wall temperature for the OTMs could have an impact on the system energy balances. The sizing of heat exchangers, number of steam tubes, and the tube placement pattern all depend on these assumptions. Future work will focus on recognizing potential heat losses and inefficiencies that affect the sizing of heat transfer surfaces.

The cost of building and operating the furnace portion of the advanced boiler is a difficult approximation because such a device has never been built. Major areas of uncertainty include manifolding of the large number of ceramic tubes, placement of the steam tubes, integration with the CO_2 capture system, and maintenance costs. It is unclear at this time how the complexity of the ceramic and steam tube network, as well as OTM replacement will affect the maintenance costs of the advanced boiler relative to a conventional boiler system. The current design also limits the turndown capability. This is mainly because the ceramic membranes must be maintained at sufficient temperature to sustain O_2 flux levels.

The CO_2 capture system is well understood in terms of performance and cost. The numbers presented here are scaled up from smaller units and would require accurate quotes to obtain a more accurate estimate. Also, the current design assumes very few diluents in the exhaust stream. The addition of diluents such as O_2 and N_2 from furnace air leaks and too much excess O_2 make the exhaust more difficult to compress, thus the system would require additional unit operations to maintain the desired product purity.

CONCLUSIONS

A design for an advanced boiler with CO_2 capture based on the criteria set forth by the CCP refinery scenario has been presented. The objective was to size and design such a system based on a given set of requirements, and compare the advanced boiler to a conventional air-fired gas boiler system.

The Praxair advanced boiler design consists of a furnace in which the fuel and exhaust gas products pass over OTMs arranged perpendicular to the flow direction. The OTMs are supported on tubes and manifold together such that each tube is fed from a common air source. Steam tubes are present along the entire length of the furnace to maintain the OTM surface temperature at the design level. The exhaust then moves onto a heat recovery system to preheat the incoming air and feed water. Finally, the spent exhaust is purified and compressed through a series of compressors and coolers to produce a supercritical CO_2 product.

Based on the current design, approximately 13 MW (43 MMBTU/h) less fuel is required in the Advanced Boiler relative to the conventional air-fired boiler sized for this case. However, because of the significant pressure drop across the OTM manifold, a large compressor or blower is required to feed air to the advanced boiler. This blower requires about 4 MW (14 MMBTU/h) of additional energy, thus the advanced boiler still shows an advantage in efficiency over the conventional boiler. The addition of the CO_2 capture system requires another 4.2 MW (14 MMBTU/h) of energy and 0.3 m^3/s (5000 gpm) of cooling water. The addition of the CO_2 capture system to the advanced boiler also shows an energy efficiency gain over the conventional boiler.

The analysis above shows that based on the economic analysis conducted to date, a boiler with integrated ceramic membranes has the potential for substantial capital and operating cost savings when CO_2 capture is required. The capital cost savings are estimated to be greater than 60%, and the CO_2 capture energy cost savings are approximately 80%. In the case of a more conventional boiler without CO_2 capture, the energy savings can potentially pay for the incremental cost of the OTM boiler in approximately 2 years.

RECOMMENDATIONS

After examining a potential design and cost estimate for the advanced boiler with CO_2 capture, there appears to be potential for technical success as well as an economic benefit over existing systems. Future recommendations for the project include:

- Continued development of robust ceramic membrane materials and fabrication methods for those materials.
- Construction of laboratory and pilot-scale advanced boilers to understand thermal integration and operational issues associated with OTMs in furnaces.
- Development of detailed models to predict OTM behavior, heat transfer within the furnace, CO_2 capture process optimization, and the impact of these physical changes on the process economics.

NOMENCLATURE

CCP	CO_2 Capture Project
FGR	flue gas recirculation
HHV	higher heating value
IGCC	integrated gasification combined cycle
ITM	ion transport membrane
LHV	lower heating value
MIEC	mixed ionic–electronic conductors
OTM	oxygen transport membrane
scfh	standard cubic feet per hour
SELIC	solid electrolyte conductor

ACKNOWLEDGEMENTS

This paper was prepared with the support of the US Department of Energy, under Award No. DE-FC26-01NT41147. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.

REFERENCES

1. H. Kobayashi, R. Prasad, A review of oxygen combustion and oxygen production systems, Proceedings of Forum on High Performance Industrial Furnace and Boiler, March 8–9, Tokyo, Japan, 1999, pp. 74-1 to 74-78.
2. L.E. Bool III, B. Van Hassel, *United States Department of Energy Proposal* DE-PS26-99FT40613, 2000.
3. L.E. Bool III, H. Kobayashi, *United States Patent* 6,394,043, 2002.
4. L.E. Bool III, H. Kobayashi, *United States Patent* 6,382,958, 2002.
5. L.E. Bool III, H. Kobayashi, *United States Patent* 6,562,104, 2003.
6. HYSYS v3.0.1 (Build 4602), Hyprotech Ltd., Copyright 1995–2002.