ADVANCED OXYFUEL BOILERS AND PROCESS HEATERS FOR COST EFFECTIVE CO_2 CAPTURE AND SEQUESTRATION

ANNUAL TECHNICAL PROGRESS REPORT

For Reporting Period Starting January 1, 2003 and Ending December 31, 2003

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ABSTRACT:

This annual technical progress report summarizes the work accomplished during the second year of the program, January-December 2003, in the following task areas: Task 1 – Conceptual Design, Task 2 – Laboratory Scale Evaluations, Task 3 – OTM Development, Task 4 - Economic Evaluation and Commercialization Planning and Task 5 - Program Management.

The program has experienced significant delays due to several factors. The budget has also been significantly under spent. Based on recent technical successes and confirmation of process economics, significant future progress is expected.

Concepts for integrating Oxygen Transport Membranes (OTMs) into boilers and process heaters to facilitate oxy-fuel combustion have been investigated.

OTM reactor combustion testing was delayed to insufficient reliability of the earlier OTM materials. Substantial improvements to reliability have been identified and testing will re-commence early in 2004.

Promising OTM material compositions and OTM architectures have been identified that improve the reliability of the ceramic elements.

Economic evaluation continued. Information was acquired that quantified the attractiveness of the advanced oxygen-fired boiler. CO_2 capture and compression are still estimated to be much less than \$10/ton CO_2.

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A. Executive summary

The breakdown of the program work consists of the following five major tasks:

Task 1. Conceptual Design
Task 2. Laboratory Scale Evaluation
Task 3. OTM Development
Task 4. Economic Evaluation and Commercialization Planning
Task 5. Program Management

Task 1 work is focused on developing conceptual designs for industrial boilers. A number of design concepts were generated during the first year of the program. During the second year of the program, more detailed design concepts of reactive purge systems were developed.

Combustion reactor laboratory scale evaluations (Task 2) efforts are behind schedule due to insufficient reliability of the ceramic elements in the reactive purge combustion environment. Substantial improvements to the ceramic materials have been made and testing will re-start early in the third year of the program.

Oxygen transport membrane (OTM) development work in this program (Task 3) is also delayed. The original OTM material selections were discarded. New candidate materials have been tested in other programs that have similar conditions to the advanced oxy-fuel boiler with substantial success. These materials are now ready to be tested in this program. In addition, changes to the architecture are being incorporated into manufacturing these elements in accordance with specific design requirements for combustion.

Economic evaluation (Task 4) continued. Information was acquired that quantified the attractiveness of the advanced oxygen-fired boiler. CO_2 capture and compression are still estimated to be much less than $10/ton CO_2.

B. Experimental and modeling initiatives

The overall goal of this program is to develop and demonstrate the integration of novel ceramic Oxygen Transport Membranes (OTMs) in a combustion process in order to enhance boiler or process heater efficiency and facilitate carbon dioxide recovery. The integration of OTMs into a combustion system facilitates oxy-fuel combustion at a substantially reduced cost of supplying oxygen compared to the cost associated with traditional air separation units. Over the last three decades, oxy-fuel fired combustion systems have demonstrated increased efficiency, reduced pollutant emissions, and improved productivity/throughput [1].

Praxair's integrated combustion concept integrates air separation using OTMs directly with the combustion process. The basic layout is illustrated in Figure 1. Preheated air enters the retentate side of the OTMs, and a driving force for oxygen transport is established due to the chemical potential difference of the combustible species. Oxygen is then reacted with a fuel and the heat of combustion is utilized to maintain sufficient temperature to activate the OTMs. The heat release is further controlled by incorporating steam tubes, thus creating steam as a product. The OTM based combustion system also results in flue gas containing only CO_2, H_2O and a limited amount of inert gas (e.g., N_2) that was contained in the starting fuel, hence the flue gas can be readily compressed to capture CO_2 for subsequent sequestration.

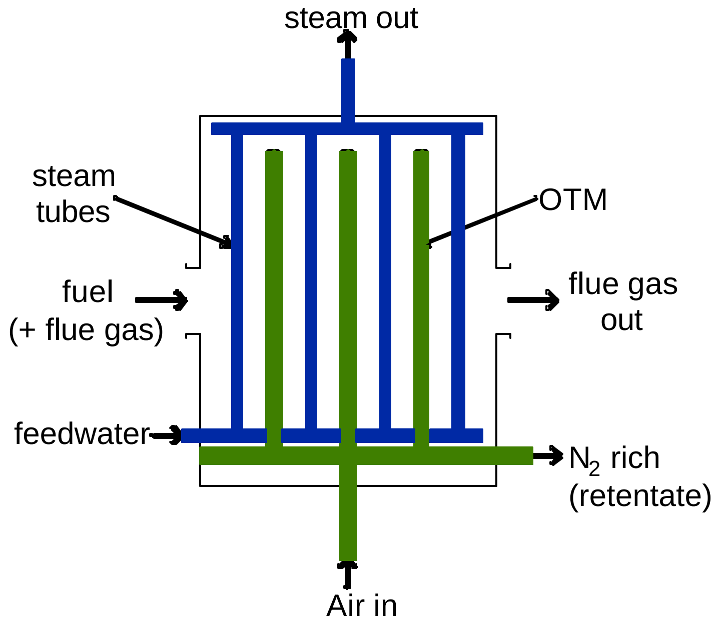

Figure 1. Fundamental layout of an OTM boiler.

B.1 Conceptual design (Task 1): Modeling

The objective of this task is to develop conceptual designs for integrating (Oxygen Transport Membranes) OTMs in boilers and process heaters to facilitate economic oxy-fuel combustion. A set of computational tools will be developed to aid in the design process. These modeling tools will be used in laboratory scale, pilot scale, and operational scale boiler design and economic evaluation.

During this reporting period, the focus was to develop a model of the overall OTM boiler system with CO_2 capture. A schematic representation of this system is illustrated in Figure 2. The system consists of (i) a furnace section in which steam is produced, (ii) a heat recovery section to increase the system efficiency, and (iii) a exhaust compression system to capture the CO_2 by compressing the flue gas from the boiler.

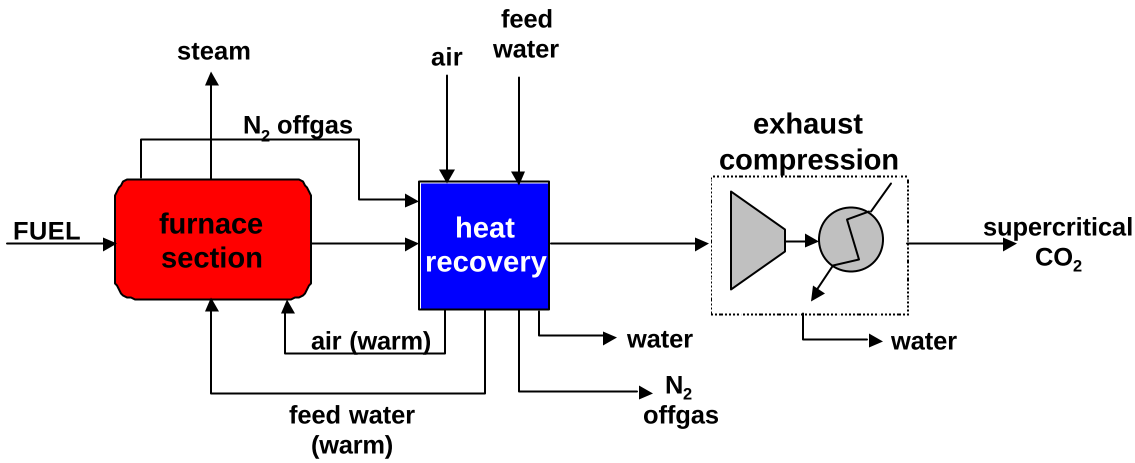

Figure 2. Overall layout of the OTM boiler system with CO_2 capture.

B.1.1 Compartmentalized macroscopic boiler model

A global network model of an OTM integrated boiler was developed to estimate boiler size for various design parameters. The boiler was modeled by dividing the system into cross section modules, in which each module contained a row of OTM tubes. Material and energy balances are performed in each module simultaneously to solve for compositions, temperature, pressure, and overall furnace length.

Using this macroscopic model, the size and design parameters of various boilers have been estimated. The model estimates the overall furnace size, number of OTM tubes, number of steam tubes, and furnace temperature profile. The information gathered from the model was then used to estimate boiler costs as part of the economic analysis.

B.1.2 Heat recovery system model

A substantial amount of heat remains in the boiler flue gas and the N_2 rich retentate from the OTM tubes. This heat can be partially recovered by using a series of heat exchangers to preheat the feed air, water, and/or fuel. The heat recovery process was modeled using the program HYSYS 3.0.1 [2] via an iterative process involving the compartmentalized boiler model. The information calculated with the model was then used to size and cost heat exchange equipment based in the process input parameters.

B.1.3 Exhaust compression cystem for CO_2 capture

In traditional air-fired boilers, the capture of CO_2 from flue gas is a complicated and expensive process. This is mainly due to the low partial pressure of CO_2 and large quantity of N_2 in the flue gas. However, the flue gas from an oxy-fuel fired boiler, such as the OTM boiler, is essentially CO_2 and H_2O. Thus, the flue gas can be compressed and cooled in a process that is less complex than a traditional amine based absorption system that would be used on an air-fired boiler.

A model of an exhaust compression system for the OTM boiler has been developed to capture CO_2 as a liquid of supercritical product. Model calculations were performed using HYSYS 3.0.1 in which the incoming flue gas stream properties depend on the outcome of the heat recovery system model. The outcome from the model was then used to size and cost the necessary equipment to capture CO_2 from the OTM boiler.

B.1.4 Advanced modeling using commercial CDF software

A general purpose CFD (computational fluid dynamic) computer code (CFX) developed and marketed by AEA Engineering Software Inc., will be applied to selected systems. The CFD modeling will focus on understanding boiler subsystems (e.g., flow profiles around tube banks). One major purpose of this modeling subtask is to recognize potential operating challenges and suggest improvement or design options. This subtask will also require the development and integration of subroutines necessary to describe the combustion and transport processes occur at and near the OTM tubes.

B.2 Laboratory scale evaluation (Task 2): Experimental

The experimental work to be carried out within this task involves the design, construction and commissioning of both single and multi-tube reactors that simulate environments likely to be experienced by the OTM tubes in the integrated combustion application. Once commissioned, the reactors will be used both to validate computer models and to ultimately qualify OTM materials and modules and elements of the proposed conceptual designs.

Single tube furnaces that are already in existence at Praxair will be used to evaluate ideal boiler conditions. These single tube reactors will evaluate basic tube performance based on temperature, pressure, OTM material, and fuel composition.

A multi-tube bench scale reactor is currently in the design stage. The objective of building this system is to understand the effects of tube arrangements, fuel composition, and heat transfer mechanisms in an OTM furnace environment. This reactor will consist of 3-6 OTM tubes that may be arranged in a variety of configurations. The test fuels will be natural gas, H_2, CO, and mixtures of these components. The reactor will incorporate flue gas recirculation or simulated flue gas recirculation by direct injection of combustion products from an external combustion source. Water cooled tubes will be present in the reactor to control the temperature of the gas and OTM surface temperature.

The testing of the single and multi-tube reactors will be in conjunction with further OTM materials development (see Section B.3). Material issues encountered in the reactor environment will be addressed in the material development portion of the program.

B.3 OTM development (Task 3): Experimental and modeling

Material and composite development work has been undertaken in a different program. The learnings from the other program are directly transferable to this program. The first composite tubular elements suitable for the ceramic advanced boiler are being fabricated at the Praxair manufacturing facility in Indianapolis using patented technology.

Modeling work to simulate the oxygen transport through multi-layered components has begun. Simple excel models are used in conjunction with Fortran models.

C. Results and Discussion

C.1 Conceptual design (Task 1): Results and discussion

C.1.1 OTM purge technique

In order to separate oxygen from air by utilizing OTMs, the membranes must be hot [1500-2000^{o}F (800-1100^{o}C)], 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 oxygen transport membrane are *gas purge* and *reactive purge* [3]. The reactive purge method [Figure 3a)] 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 3b)], 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 substantially less than the reactive purge case.

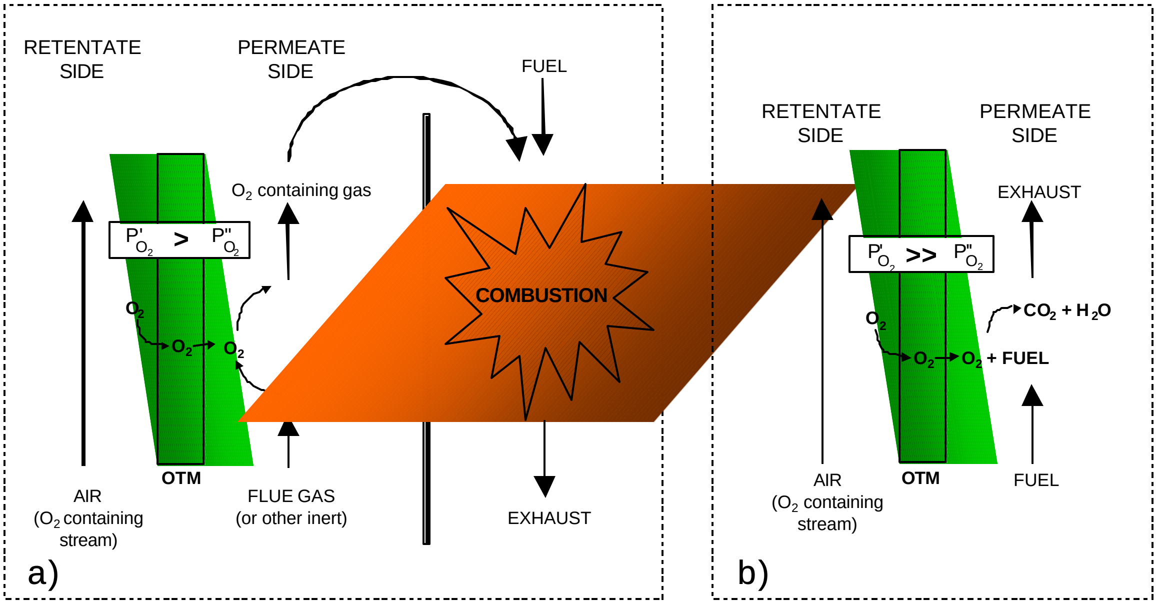

Figure 3. a) Reactive purge and b) gas purge methods for removing O_2 from the permeate side of an OTM membrane.

The choice of the purge technique for the OTMs has a strong impact on the boiler design. Table 1 is a list of some of the key issues associated with a gas fired boiler design, and the columns on the right indicate which purge technique is advantageous in addressing the issues. For an OTM boiler burning a gaseous fuel, the reactive purge technique has more advantages than the flue gas purge technique. Thus, the designs considered from this point forward will revolve around a reactive purge OTM combustion system.

Table 1. Advantages of OTM purge techniques for the key issues associated with boiler design.

Key Issues	Flue Gas Purge	Reactive Purge
O_2 Flux		✓
boiler size		✓
Tube life/reliability	✓	
Temperature control	✓	
operating cost		✓
capital cost		✓

✓ = advantage

C.1.2 <u>Modeling results: Case study</u>

The work described below was completed outside of this cooperative agreement, but is included due to its direct applicability to this program.

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 4. 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.

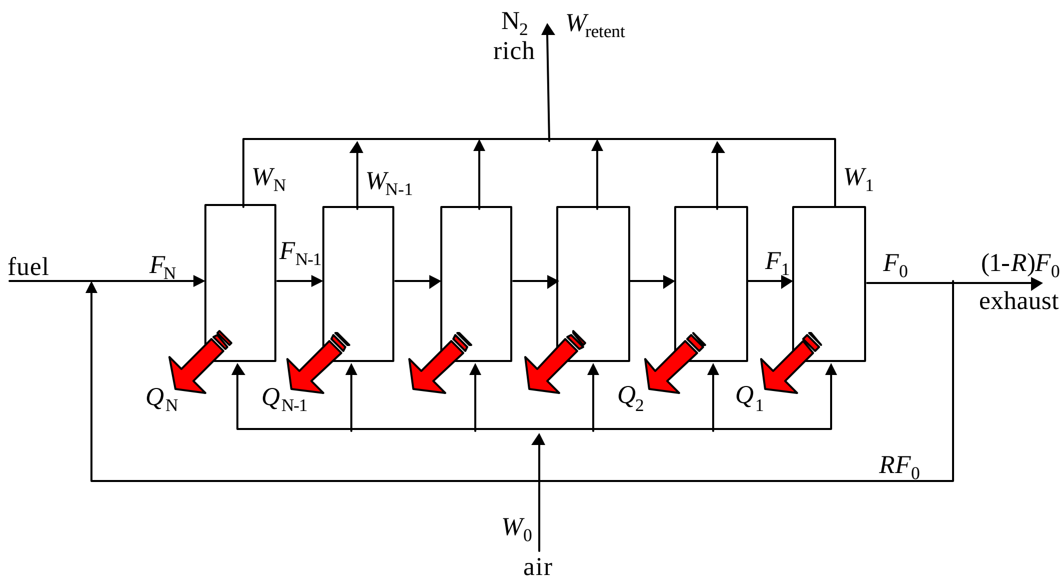

Figure 4. Module representation of the furnace section of the OTM boiler.

In order to simplify the calculations, a number of assumption 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.

The global network model was combined with the heat recovery section model in order to calculate the system temperatures and efficiency in an iterative fashion. An initial guess for the temperatures was obtained from the network model, which was then applied to the heat recovery model illustrated in Figure 5, and solved using HYSYS. The new temperatures were then used to resolve the network model and the process repeated until the desired tolerance was achieved.

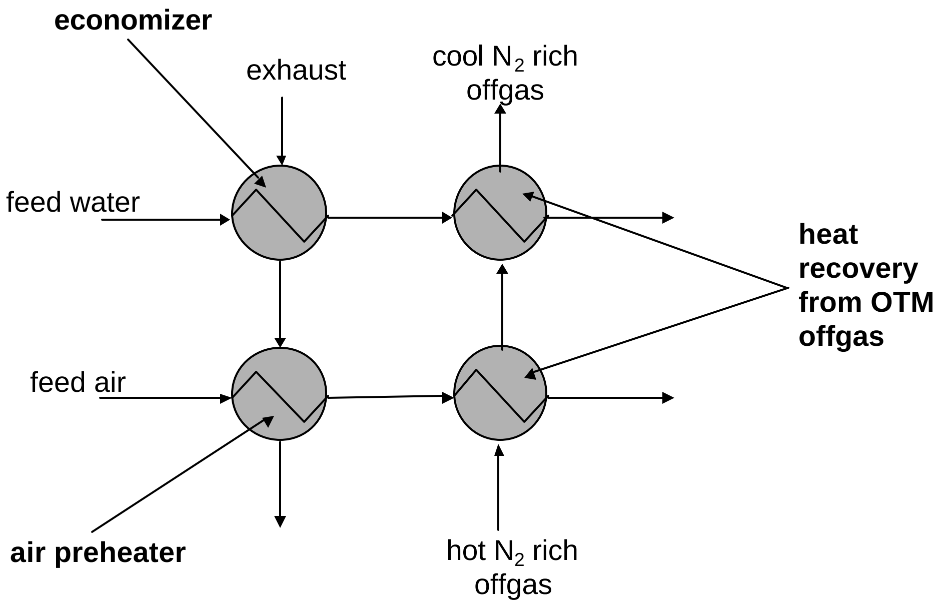

Figure 5. Heat recovery model for the OTM boiler.

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 6. The compression of the exhaust gas was modeled using HYSYS 3.0.1.

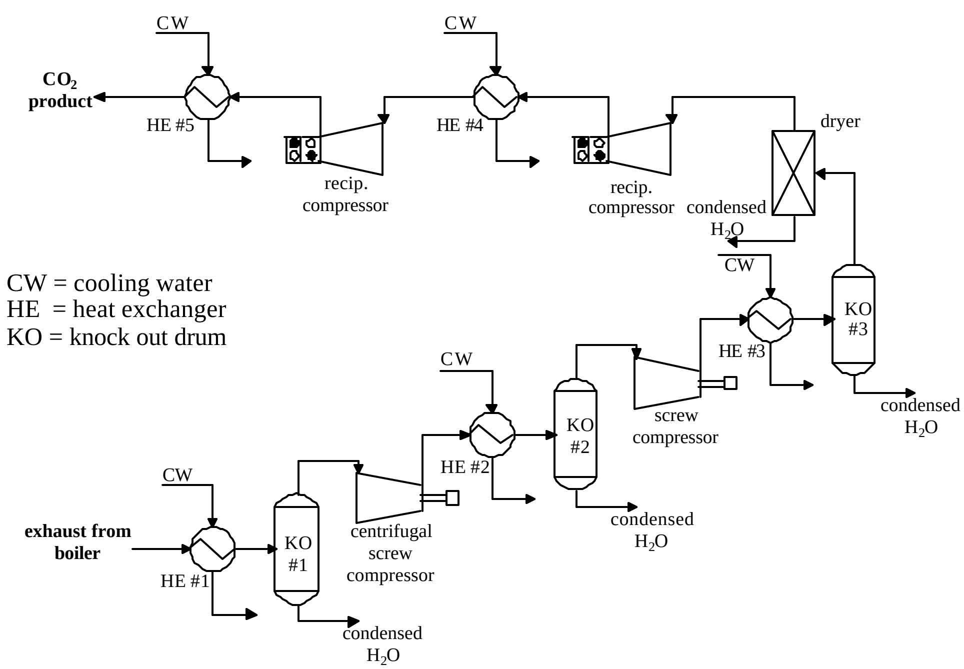

Figure 6. Flow diagram of the exhaust compression system

Modeling results to date have focused on a case study involving a hypothetical air-fired boiler that would be replaced by an OTM boiler with CO_2 capture. The parameters of the hypothetical boiler are:

- 500,000 lb/hr (63 kg/s) steam production
- natural gas fueled
- products of combustion move in a cross-flow pattern relative to the OTM and steam tubes [4]
- zero air leakage into the furnace
- 75% of the O_2 in the incoming air is transported through to the permeate side of the membrane

Economic results for this case study are presented in Section C.4. Refinement of the model as well as the creation of more detailed heat transfer models are currently in the development phase.

C.2 Laboratory scale evaluations (Task 2): Results and discussion

Existing Praxair single tube reactors have been modified for use in this program. Initial shake downs have occurred and a safety review is scheduled. Composite tubes are prepared and ready for testing once the reactors have completed their safety review.

The current focus of the laboratory scale evaluation is to build a multi-tube reactor. The reactor will consist of 3-6 OTM tubes and will have the potential to position the tubes in a variety of configurations. Cooling water tubes will be present within the reactor to simulate steam tubes and control the OTM surface temperature. A portion of the flue gas will be recirculated, mixed with the fuel, and the mixture may be further preheated before entering the reactor. The reactor is scheduled to be completed and operation by the end of 2004.

C.3 OTM development (Task 3): Results and discussion

Earlier materials that were considered suitable for the ceramic advanced boiler have been discarded due to insufficient reliability. Work conducted in a separate Praxair program has identified two candidate compositions for use in the boiler program. These materials have been tested for reliability in other programs and show promise. Further development work based on these compositions and subsequent reliability and performance testing is required during the remainder of the budget phase to verify the suitability of the material in the harsh combustion environment.

C.4 Economic evaluation and commercialization planning (Task 4): Results and Discussion

The work described below was completed outside of this cooperative agreement, but is included due to its direct applicability to this program.

A cost analysis was performed on the case study described in Section C.1 to investigate the economics associated with the OTM boiler compared to a conventional air-fired boiler in which both system are required to capture CO_2. Using the model described previously, the system size was calculated and the associated costs of the equipment was estimated. The results of this analysis appear in Table 2.

Table 2. Cost comparison of boiler options for system costs and CO_2 capture energy

Costs	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**
Operating Costs		
Annual fuel cost @ $3.5/MM BTU ($0.0033/MJ)	$21,000,000	$19,700,000
Annual power cost @ $0.045/kWh	$53,000	$1,500,000
Operating cost savings with condensing heat exchanger	-	$(1,300,000)
Total boiler operating cost	**$21,100,000**	**$19,900,000**
CO_2 Capture Costs		
Annual steam @ $3.5/MM BTU	$4,100,000	
Annual power @ $0.04/kWh	$2,900,000	$1,500,000
Annual chemicals	$1,500,000	
Total CO_2 cap. Op. Cost	**$8,500,000**	**$1,500,000**

The installation of a new OTM boiler with CO_2 capture shows approximately a 60% savings in capital versus the installation of a new air-fired boiler with an appropriate CO_2 capture system. The operating cost of the OTM boiler alone (not including CO_2 capture) shows a 6% cost savings compared to a conventional air-fired system. The cost savings come about primarily because part of the latent heat of water can recovered by utilizing condensing heat exchanger technology. Also, by optimizing the air flow system, Praxair believes that the operating cost of the OTM boiler can be substantially reduced leading to a larger operating cost savings. Finally, the operating cost of the CO_2 capture system alone associated with the OTM boiler shows an 80% savings compared to an absorption based system for an air-fired boiler.

These costs can also be represented in terms of the cost per ton of CO_2 or carbon avoided. Table 3 illustrates the cost of installing three different systems based on the incremental cost addition compared to a new air-fired boiler: (1) an OTM boiler without CO_2 capture, (2) a CO_2 capture system for the conventional boiler, and (3) an OTM boiler with a CO_2 capture system. For the case study investigated, the installation of an OTM boiler would reduce the CO_2 emissions by over 20,000 tons per year and reduce the overall annual cost compared to the equivalent conventional boiler. The cost to remove CO_2 from the conventional boiler is approximately $38 per ton CO_2 or $139 per ton of carbon. The installation of the OTM boiler with CO_2 capture reduces this cost substantially, and the cost to capture carbon is close to the DOE goal of $10/ton carbon sequestered. As previously stated, optimization of the system should lead to increased cost savings and bring the carbon capture price to within the prescribed limits.

Table 3. Incremental cost comparison for CO_2 and carbon avoided based on the OTM boiler and CO_2 capture system additions.

	OTM Boiler NO CO_2 capture	Conventional Boiler CO_2 capture system	OTM Boiler w/ CO_2 capture
CO_2 Reduction (ton/yr, based on natural gas)	20,700	330,000	330,000
Incremental annualized capital (12%, 20 year life)	$ 330,000	$ 4,080,000	$ 1,140,000
Incremental annual operating cost	$ (1,200,000)	$ 8,500,000	$ 300,000
$/ton CO_2 avoided		**$ 38**	**$ 4**
$/ton carbon avoided		**$ 139**	**$ 16**

C.5 <u>Program Management (Task 5)</u>

The program suffered early delays principally due to the insufficient reliability of the OTM materials. Work over the past year in other programs has identified candidate materials that are now ready to be tested. As a result of the lack of materials, work on the laboratory scale reactors was considered inappropriate. Consequently, the program is significantly under budget at this time. Progress and corresponding expenditure is expected to pick up due to the identification of suitable candidate materials in the next year. We anticipate being back on schedule by the end of this phase of the program and all program targets will be met.

D. Conclusions

Process and economic analysis confirm that the advanced oxyfuel boiler offer significant advantage over competitive technology. In particular, the opportunity to capture CO_2 at an incremental cost of as low as $4/ton is extremely attractive. Problems with reliability have been work on over the past year and significant tube testing is expected in the following year.

E. Future Work

During the next year, work on conceptual design and process economics will continue. Oxygen flux and combustion experiments on single ceramic OTM tubes will begin to demonstrate oxy-fuel combustion at commercially interesting oxygen fluxes. A multi-tube OTM reactor will be constructed in the second half of the year for self-sustaining combustion testing in the final year of the program.

F. References

[1] H. Kobayashi and R. Prasad, "A Review of Oxygen Combustion and Oxygen Production Systems", Proceedings of Forum on High Performance Industrial Furnace and Boiler, March 8-9, 1999, Tokyo, Japan, pp74-1 to 74-8.

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