

**OXYGEN TRANSPORT
MEMBRANE (OTM) AIDED
OXYGEN ENHANCED
COMBUSTION**

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FEASIBILITY ANALYSIS AND FINAL EISG REPORT

**ENERGY INNOVATIONS SMALL GRANT
(EISG) PROGRAM**

INDEPENDENT ASSESSMENT REPORT (IAR)

**OXYGEN TRANSPORT MEMBRANE (OTM) AIDED OXYGEN
ENHANCED COMBUSTION**

EISG AWARDEE

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2.4 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to \$75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Energy Systems Integration

The EISG Program Administrator is required by contract to generate and deliver to the Commission an Independent Assessment Report (IAR) on all completed grant projects. The purpose of the IAR is to provide a concise summary and independent assessment of the grant project in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions. The IAR is organized into the following sections:

- Introduction
- Objectives
- Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Appendices
 - Appendix A: Final Report (under separate cover)
 - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the Commission's Web site at:

<http://www.energy.ca.gov/research/innovations>

or contact the EISG Program Administrator at (619) 594-1049, or email at:

eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at

<http://www.energy.ca.gov/research/index.html>.

Oxygen Transport Membrane (OTM) Aided Oxygen Enhanced Combustion

EISG Grant # 00-29

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Introduction

Modern combustion turbines in California power plants use lean, premixed combustion to significantly reduce air pollution from oxides of nitrogen (NO_x) and carbon monoxide (CO). The flame stability in the combustor limits the degree to which NO_x can be reduced. If the turbine is excessively starved for fuel, it will stop running. Before flame extinction occurs, flame instability causes a phenomenon called “rumble,” which results in serious damage to the engine. This introduces a practical lower limit on how lean the fuel-air mix can be, called the “lean limit.” That in turn results in NO_x production that cannot be lower than a certain minimum for any given combustion turbine using air as the oxidizer.

California power plants could reduce the creation of NO_x pollutants if the flame stability was improved to produce a lower lean limit. Further, improved flame stability could reduce damaging turbine “rumble” and life-limiting hot spots at the turbine inlet. Since even the cleanest gas-turbine power plants can produce over 200 tons per year NO_x per 500 MW, there is a great incentive to reduce the quantity of this pollutant going into the atmosphere. Additionally, improved flame stability can result in high engine efficiency.

Engineers have shown that adding oxygen to the combustion air (oxygen-enhanced combustion (OEC)) results in stable combustion at a lower lean limit. The key challenge facing OEC is the significant cost of oxygen enrichment. This project studied the feasibility of using dense, high-temperature, solid-oxide membranes (oxygen-transport membranes (OTM)) to produce oxygen *in situ*, thus improving the quality of the combustion air, as illustrated in Figure 1. The researcher proposed using high-quality oxygen-transport membranes and waste heat from the exhaust-gas stream to obtain the oxygen.

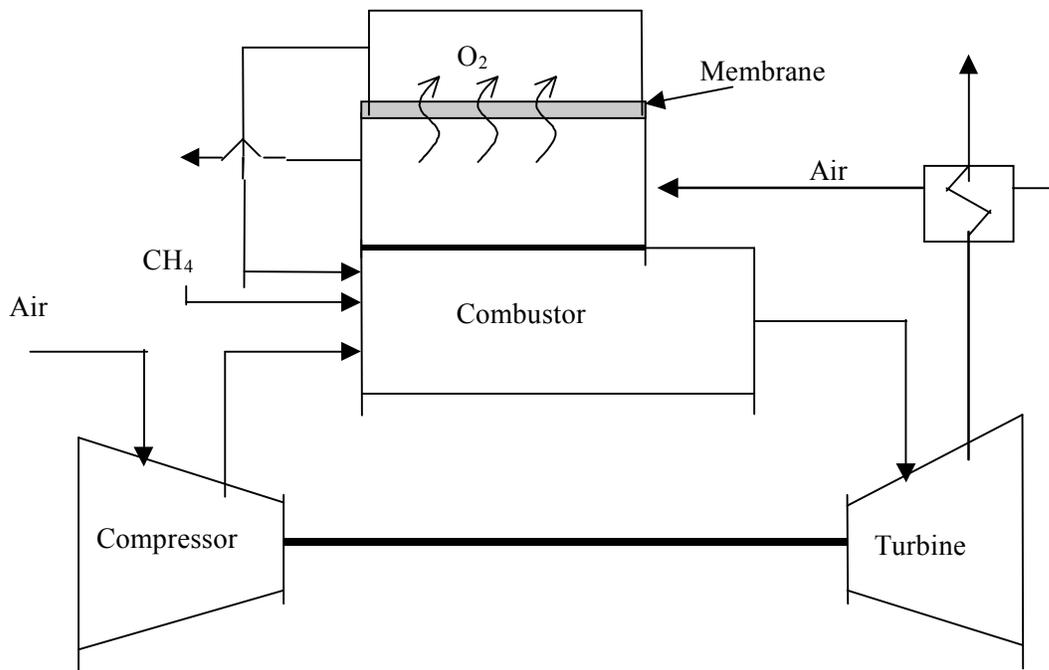


Figure 1. Schematic of the OEC using an oxygen-transport membrane. In the illustration air is compressed, heated in the combustor, and expanded through the turbine, as is typical of all gas turbines. Next, however, the turbine's hot exhaust is routed through a heat exchanger, heating additional air, which is then routed through the OTM construct. The OTM allows oxygen to pass to the combustor, while the rest of the air is expelled. Note that the system will not work as illustrated because low-pressure oxygen feeds directly into the high-pressure gases entering the combustor. Instead, the oxygen should be routed to the compressor.

Objectives

The goal of this project was to determine the feasibility of using oxygen-transport membranes to produce oxygen *in situ* for use in an OEC combustor for gas-turbine electricity generation. The researchers established the following project objectives:

1. Determine the technical feasibility of coupling oxygen-transport membranes (OTM) with oxygen-enhanced combustion (OEC). Determine stability characteristics of membranes in the OEC environment.
2. Determine the combustion stability of the OTM/OEC hybrid concept.
3. Determine the formation of pollutants, with particular emphasis on NO_x emissions. Quantify the potential for attaining NO_x emissions in the single-digit ppm range.
4. Determine combustion-stability and pollutant-formation characteristics for oxygen lancing. This is one of the techniques industry uses for the implementation of OEC.
5. Determine the potentials of the OTM/OEC technology for improving the efficiency of gas turbines to values in excess of 35%.

Outcomes

- 1) The researcher prepared a number of dense solid-oxide oxygen-conducting membranes made of $\text{SrCo}_{0.5}\text{FeO}_3$ perovskite material, and tested them for oxygen-permeation characteristics. The researcher also tested them under both inert and reactive conditions. The membranes prepared showed satisfactory oxygen permeability and good stability during the permeation studies, both in the presence of inert and reactive sweeps.
- 2) O_2 addition increased laminar flame speed and, therefore, enhanced flame stability. This was due to the progress of the branching reaction as the O_2 concentration increased.
- 3) Analysis of the NO_x structures revealed that O_2 enrichment resulted in reduced NO_x production for the same flame temperature. Single-digit NO_x production was not reported. Oxygen addition appeared to limit the emission of other pollutants. Studies of fuel-rich flames, for example, revealed a significant reduction of the maximum CO mole fraction, $(X_{\text{CO}})_{\text{max}}$, as X_{O_2} increases for flames with constant T_{max} . This reduction was due to the interaction downstream of the premixed flame between the fuel-rich premixed and the non-premixed flame.
- 4) Both theoretical and experimental data showed that oxygen lancing beneficially reduced CO/ NO_x emissions when oxygen-enhanced and non-enhanced tests were run with the same maximum flame temperature.
- 5) Design calculations indicated that turbine efficiencies as high as 46% can be achieved through the implementation of OTM/OEC technology. The degree of improvement is difficult to discern, since the efficiency of the engine under evaluation appeared to be between 42% and 43% before the addition of the OTM/OEC technology.

Conclusions

1. These membranes are highly permeable to oxygen under conditions similar to those in the OEC combustion environment. The researcher showed oxygen permeability of these membranes under reactive conditions to be significantly higher than those attained in inert environments.
2. Results on flame propagation demonstrated that oxygen enrichment could enhance combustion stability: the same flame temperature increased laminar flame speeds and extended flammability limits. This was caused by the effect of oxygen concentration on the main branching reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. Under certain enriched conditions, the researcher found that oxygen addition acted as a heat sink to reduce flame temperatures. Higher oxygen concentration also increased laminar flame speed, thus enhancing the progress of the branching reaction.
3. Analysis of the NO_x structures revealed that oxygen enrichment can reduce NO_x production for the same flame temperature. Lower NO_x production is caused by the synergistic effect of reduced flame temperature and reduced N_2 concentration.

4. The researcher found a significant reduction of the maximum CO mole fraction, $(X_{CO})_{max}$, as X_{O_2} increased for flames with constant T_{max} . The researcher hypothesized that this reduction comes from the interaction between the fuel-rich premixed and the non-premixed flame established downstream of the premixed flame. More specifically, the reduction of the equivalence ratio required to maintain a constant T_{max} as X_{O_2} increases, is responsible for the reduction of both $(X_{CO})_{max}$, and $(X_{NOx})_{max}$.
5. Design calculations indicated that turbine efficiency increased with the degree of oxygen enrichment. That depended on the quality of membranes utilized. Membranes with poor separation characteristics or lower permeability showed poor performance, as their operation required additional energy beyond the available waste heat. In fact, use of inferior-quality membranes was likely to result in a decrease in turbine efficiency.

Oxygen-enhanced combustion is a proven technique. This project was undertaken in order to prove the feasibility of using oxygen-transport membranes to produce oxygen *in situ* for use in oxygen-enhanced combustion for gas turbines. The fundamental feasibility of this concept has been proven. OTMs can function in conditions similar to the OEC environment. It remains to be seen if OTMs can extract a sufficient volume of oxygen from the exhaust stream at a high enough rate to be useful in the gas turbine.

Recommendations

The use of solid-oxide membranes in power-generation applications has been proven technically feasible. In order to bring the technology to the commercial stage the following tasks should be conducted:

1. Develop inexpensive, tubular, solid-oxide membranes and demonstrate the OTM/OEC concept in a scaled-up membrane reactor/combustor configuration.
2. Test the long-term (>1 year) stability of tubular membranes.
3. Carry out an extensive economic evaluation of the technology, including a detailed market survey.

After taking into consideration: (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow-on funding within the PIER program.

Receiving follow-on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

Benefits to California

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution systems

- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. The researcher projects at least a 1.5% increase in the efficiency of gas turbines and a 20%–60% decrease in NO_x emissions for those turbines using lean, premixed combustion. The baselines for these estimates are not clear, therefore it is not possible to estimate the overall impacts on the California ratepayer.

Other researchers have shown that oxygen-enhanced combustion in gas-turbine engines results in higher turbine efficiency or lower levels of NO_x and CO emissions. This study demonstrated that similar results can occur when high-quality oxygen-transport membranes and waste heat are used to obtain the oxygen from the exhaust-gas stream. This could benefit the ratepayer through a low-cost implementation of oxygen-enhanced combustion resulting in higher turbine efficiency or lower levels of regulated emissions.

Overall Technology Development Assessment

As the basis for this assessment, the Program Administrator reviewed the researcher's overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The target markets for this technology are primarily boiler and power plant industries as well as high-temperature furnaces such as glass and steel furnaces, incinerators, etc. The project has performed a preliminary market survey of various industrial representatives and a number of potential users. There are no foreseen regulatory or legal barriers to this technology.

Engineering/Technical

This project has demonstrated that it is feasible to filter oxygen from air using only the heat available in a gas-turbine exhaust. There remains the technical question of the volume and production rate of oxygen needed for the OTM/OEC concept. This is to be demonstrated in a scaled-up membrane reactor/combustor configuration. This project has not developed a requirements specification. A small-scale pilot plant is expected to cost over \$300,000 and require three to five years to complete. Several developments in tubular membranes must precede testing of any pilot plant.

Legal/Contractual

The researcher has performed a patent search on the technology but has not filed for patent protection due to the preliminary nature of the research.

Environmental, Safety, Risk Assessments/ Quality Plans

The state of this research is too preliminary to justify expending extensive effort performing detailed quality planning. Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental.

Production Readiness/Commercialization

This university research group is aware of the need for an industrial partner to enable the further development of this product. Although no commercialization plan has been written to date, this project has been jointly proposed with an industrial partner to further the technical development through the U.S. Department of Energy funding. Commercialization risks are currently being evaluated.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to FAR 00-29

**ENERGY INNOVATIONS SMALL GRANT
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EISG FINAL REPORT

OTM AIDED OXYGEN ENHANCED COMBUSTION

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Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619)594-1049 or email eisgp@energy.state.ca.us.

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Abstract

O₂ lancing, one of the industrial techniques for implementing oxygen-enhanced combustion (OEC), can potentially result in stable combustion with reduced NO_x emissions. The key technical challenge facing lancing (and OEC in general) is the significant cost of O₂ enrichment. The present work reports results from a study of methane OEC, in which the O₂-enrichment of air is implemented *in situ* using dense, high-temperature mixed-conducting solid-oxide membranes. We report on the preparation and characterization of these membranes, and on the fundamental combustion studies of the relevant reactive mixtures, including the effect of O₂ lancing on the NO_x and CO emissions of fuel-lean and fuel-rich CH₄/air premixed flames. The potential of the OTM/OEC technology for improving gas turbine efficiency has also been determined. The technical feasibility of coupling oxygen transport membranes (OTM) with oxygen-enhanced combustion (OEC) has been studied, and the stability characteristics of membranes in the OEC environment have been determined. As part of this effort, solid oxide membranes were prepared and their oxygen permeation was measured in a membrane system. The O₂ permeabilities in the presence of a reactive sweep were significantly higher than the corresponding permeabilities measured in the presence of He as a sweep gas. Engineering calculations of the overall efficiency were also carried out and the conditions for optimal performance were determined. Generally, improvements in combustion intensity and stability can be achieved but at a cost of increased NO_x emissions, and vice versa.

Key word: solid oxide membrane, power generation, gas turbine, lean combustion, oxygen transport membranes.

Executive Summary

Introduction

The use of an O₂-enriched oxidizer in natural gas (NG) combustion stems either from the requirement to achieve high temperatures in industrial processes, or the need to enhance flame stability under fuel-lean burning conditions. O₂-enriched combustion (OEC) is a potential solution in the latter application, because increasing the O₂ content allows one to burn more stably, while maintaining the same flame temperature, an important consideration, since flame temperature is a good measure of the combustion device's energetic output. Furthermore, for the same flame temperature, O₂-enrichment offers the additional advantage of lower NO_x production due to the reduced N₂-content. OEC also shows promise in power generation for staged combustion with the O₂-enriched oxidizer involved in one of the stages.

There are other OEC beneficial effects including increased radiative heat transfer rates, enhanced power output and thermal efficiency and significant reduction in flue-gas volume. OEC flue-gas contains higher CO₂ levels, an important advantage, if CO₂ capture/recovery ever becomes an issue. Taken together these benefits give OEC an excellent long-term potential for expanded power generation applications. OEC, however, has yet to recognize its full potential due to some key concerns. For example, though OEC shows potential for lower NO_x production, the pollutant emissions during OEC, especially NO_x are affected in a complex way by the operating conditions, including pressure, temperature and degree of O₂ enrichment. Associated with OEC are, furthermore, combustion control problems, since the enhanced flame speeds present the potential of flashback. For the OEC benefits and problems to be assessed the existing rudimentary scientific understanding is not sufficient. It is important that the specific and detailed characteristics of the combustion processes involved are well understood and considered. This was one of the goals of this project, which involved the systematic study of OEC, in order to quantify the potential of O₂ enrichment for enhancing combustion stability, increasing thermal efficiency, and reducing pollutant emissions.

With OEC there is a trade-off in the operating costs between the savings in fuel, due to the improved combustion efficiencies, and the cost of O₂ enrichment. The economics/energy consumption of conventional cryogenic and adsorption technologies for O₂ separation from air are, at present, the other key factor hampering the widespread application of OEC. Membrane-based technologies have been proposed as a promising alternative. The recent technological breakthrough here, which promises to make OEC a commercial reality, is high temperature, oxygen transport membranes (OTM). These membranes have been studied at the pilot plant scale with significant success for catalytic partial oxidation to produce synthesis gas. Their use in combustion applications, though in principle rather straightforward, presents unique technical challenges that must be addressed, before one proceeds to similar scale, pilot-plant size applications. This project was initiated to address some of these technical challenges. Studies were conducted in order to identify conditions under which the combined OTM/OEC process is economically feasible.

Project Objectives

The project goal was to evaluate the technical feasibility and environmental implications of a novel technology involving an OTM/OEC hybrid concept within the context of power/energy generation. The technology envisions O₂ production to take place using oxygen transport membranes. To accomplish the goal the project addressed the following four objectives:

- 1) Determine the technical feasibility of coupling oxygen transport membranes (OTM) with oxygen-enhanced combustion (OEC). Determine stability characteristics of membranes in the OEC environment.
- 2) Determine the combustion stability of the OTM/OEC hybrid concept.
- 3) Determine pollutant formation characteristics with particular emphasis on NO_x emissions. Quantify the technology potential for attaining NO_x emissions in the single ppm digit range.
- 4) Determine combustion stability and pollutant formation characteristics for oxygen lancing, which is one of the techniques used by the industry for implementation of OEC.
- 5) Determine the potential of the OTM/OEC technology for improving gas turbine efficiency, and its potential for achieving efficiencies in excess of 35 %.

Project Outcomes

The following were the key technical outcomes of the project:

- 1) The membranes prepared show satisfactory oxygen permeability, and good stability during the permeation studies, both in the presence of inert and reactive sweeps.
- 2) O₂ addition results in laminar flame speed increase and, therefore, enhancement of flame stability. This is due to the progress of the branching reaction as the O₂ concentration increases.
- 3) The analysis of the NO_x structures revealed that O₂ enrichment can be of value, as it results in reduced NO_x production for the same flame temperature. Oxygen addition appears to have additional beneficial effects in terms of other pollutant emissions. Studies of fuel-rich flames, for example, revealed a significant reduction of the maximum CO mole fraction, $(X_{CO})_{max}$, as X_{O_2} increases for flames with constant T_{max} . This reduction was found to be caused by the interaction between the fuel-rich premixed and the non-premixed flame established downstream of the premixed flame.

- 4) Design calculations indicate that turbine efficiencies as high as 46% are potentially achieved through the implementation of OTM/OEC technology.

Conclusions

The key technical conclusions drawn from our investigation are as follows:

- Solid oxide dense oxygen conducting membranes, made of $\text{SrCo}_{0.5}\text{FeO}_3$ perovskite material, have been prepared and tested for their oxygen permeation characteristics. These membranes have been shown to be highly permeable to oxygen under conditions akin to the OEC combustion environment.
- To investigate further the feasibility of the proposed process, a number of $\text{SrCo}_{0.5}\text{FeO}_3$ membrane disks have been prepared and tested under both inert and reactive conditions. The O_2 permeabilities of these membranes under reactive conditions were shown to be significantly higher than those attained in inert environments.
- Results on flame propagation revealed that O_2 enrichment can enhance combustion stability, since for the same flame temperature, the laminar flame speeds increase, and the flammability limits are extended. This is caused through the effect of O_2 concentration on the main branching reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$. Under certain conditions of enrichment, it was found that while the O_2 addition results in flame temperature reduction, as it acts as heat sink, the laminar flame speed increases, as the O_2 concentration increases, enhancing, thus, the progress of the branching reaction.
- The analysis of the NO_x structures revealed that O_2 enrichment can be of value, as it results in reduced NO_x production for the same flame temperature. The reduction of NO_x production is caused by the synergistic effect of flame temperature reduction and N_2 concentration reduction, as more O_2 is added.
- Studies of fuel-rich flames also revealed a significant reduction of the maximum CO mole fraction, $(X_{\text{CO}})_{\text{max}}$, as X_{O_2} increases for flames with constant T_{max} . This reduction was found to be caused by the interaction between the fuel-rich premixed and the non-premixed flame established downstream of the premixed flame. More specifically, the reduction of the equivalence ratio, required to maintain a constant T_{max} as X_{O_2} increases, was found responsible for the reduction of both $(X_{\text{CO}})_{\text{max}}$, and $(X_{\text{NO}_x})_{\text{max}}$.
- Design calculations indicate that turbine efficiency increases with the degree of oxygen enrichment. The efficiency improvement depends on the quality of membranes utilized. Membranes with poor separation characteristics or lower permeability show poor performance, as they require for their operation additional energy beyond what is available through the available waste heat. In fact, use of inferior quality membranes is likely to result in a decrease in turbine efficiency.

Recommendations

The use of solid oxide membranes in power generation applications has been proven technically feasible. In order to potentially bring the technology to the commercial stage the following tasks should be conducted:

- Develop cheap, tubular solid oxide membranes, so that the OTM/OEC concept can be evaluated in a scaled-up membrane reactor/combustor configuration.
- Test the long-term (>1 year) stability of tubular membranes.
- Carry out an extensive economic evaluation of the technology, including a detailed market survey.

Public Benefits to California

The concept feasibility of the proposed OTM/OEC process has been proven. With this know-how, the technology can be potentially moved all the way from the “proof of concept” level to pilot-plant scale demonstration, and to full-scale commercialization. Power generation is the primary focus of this project. Industrial furnaces and boilers, however, also represent another important potential application. What has been learned here on the OTM/OEC technology will be of also of great value in these areas of application.

1 Introduction

1.1 Energy Problem Targeted and its Impact

The use of an O₂-enriched oxidizer in natural gas (NG) combustion stems either from the requirement to achieve higher temperatures in industrial furnaces and boilers (with either low, e.g. 21-30%, or high, e.g. 80-95%, O₂-enrichments being of practical interest), or the need to enhance flame stability (e.g., increased resistance to extinction and higher flame speeds) under fuel-lean burning conditions in gas turbines. Fuel-lean burning is the prevailing means of operation in the gas turbine industry. Fuel-lean oxidation processes, however, are often affected by heat-loss phenomena and severe aerodynamic straining, and the presence of non-equilibrium effects results in combustion stability problems, and increased emissions of unburned hydrocarbons (UHC) and carbon monoxide (CO). Oxygen-enriched combustion (OEC) is a potential solution, because increasing the O₂ content enhances the rate of the main branching reaction, i.e., $H + O_2 \leftrightarrow OH + O$ (largely responsible for the O₂ consumption and the production of the OH and O radicals) through the combined effects of the increase of the flame temperature and O₂ concentration. Being able to burn more stably, while maintaining the same flame temperature, is an important consideration, since flame temperature is a good measure of the energetic output of the combustion device. Furthermore, for the same flame temperature, O₂-enrichment offers the additional advantage of lower NO_x production due to the reduced N₂-content. The use of an O₂-enriched oxidizer is, potentially, of value to high temperature industrial furnaces and boilers, but also in the power generation environment for staged combustion with the O₂-enriched oxidizer involved in one of the stages.

There are other OEC beneficial effects. They include increased radiative heat transfer rates due to the higher flame temperatures, and enhanced power output and thermal efficiency (less heat "wasted" in heating-up the N_2 in the flue gas); and significant reduction in flue-gas volume (less N_2 in the flue gas), thus resulting in size reduction of the associated post-combustion treatment hardware. OEC flue-gas contains higher CO_2 levels, an important advantage, if CO_2 capture/recovery ever becomes a real issue (Alan and Spilburg, 1992). Taken together these potential benefits give OEC an excellent long-term potential for expanded power generation and other combustion applications (Williams et al., 1989; Chase et al., 1989). OEC, however, has yet to recognize its full potential (beyond the glass [DaSilva et al., 1994] and metal industries [Baukal, 1998], for which very high temperatures, not easily attainable by conventional combustion, are necessary) due to some key concerns. As noted above, OEC shows potential for lower NO_x production. However the pollutant emissions during OEC, especially NO_x , vary greatly, affected in a complex way by the operating conditions, including pressure, temperature, and degree of oxygen enrichment (Kuigowaki and Laurendeau, 1997). Associated with OEC are, furthermore, challenging combustion control problems, since the enhanced flame speeds present the potential of flashback into the mixture supply lines, when feed velocities fall below a critical value, which, if not properly addressed, can have severe consequences. For the benefits and problems of OEC to be assessed, a rudimentary scientific understanding of the process, as it exists today, is not sufficient. It is important that the specific and detailed characteristics of the various combustion processes involved are well understood and considered. This was one of the goals of this project, which involved the systematic study of the combustion characteristics of O_2 -enriched CH_4 /air mixtures, in order to scientifically quantify the potential of O_2

enrichment for enhancing combustion stability, increasing thermal efficiency, as well as for reducing pollutant emissions.

With OEC there is a trade-off in the operating costs between the savings in fuel, due to the improved combustion efficiencies, and the cost associated with the O₂ enrichment. The economics/energy consumption of conventional technologies for oxygen separation from air (cryogenic and adsorption methods) are, at present, the other key factor hampering the widespread application of OEC. Membrane-based technologies have been proposed as a promising alternative (Rigby and Warson, 1994). The recent technological breakthrough here, which could potentially make the application of OEC a reality, is the development of high temperature, oxygen conducting solid oxide membranes. These membranes have been studied at the pilot plant scale with significant success for catalytic partial oxidation to produce synthesis gas. Their use in direct combustion applications, though in principle rather straightforward, presents unique technical challenges that must be addressed, before one proceeds to similar scale, pilot- plant size applications. This project was intended to address some of these challenges. Detailed studies were conducted in order to identify conditions under which the process is economically feasible.

1.2 State-of-the-art

As noted above, natural gas OEC is of value to a number of industrial processes, which require higher temperatures, and for enhancing flame stability under fuel-lean conditions. O₂-enrichment is also, in addition, of practical interest in the power generation environment for staged combustion with the O₂-enriched oxidizer involved in

one of the stages. Higher temperatures are achieved, as a result of the reduced N_2 -content of the O_2 -enriched oxidizer, since N_2 is an inert gas, simply acting as a heat sink. Flame stability enhancement is a result of the increased resistance to extinction of the higher flame-speed flames achieved under such conditions. Being able to burn more stably, while maintaining the same flame temperature, is an important consideration, since flame temperature is a good measure of the combustion device's energetic output. Another key consideration is that for the same flame temperature O_2 -enrichment offers the additional advantage of lower NO_x production due to the reduced N_2 -content.

Stability of Lean-Premixed Combustion

Lean, premixed combustion is commonly practiced in the gas turbine industry, because of its potential for reducing emissions of key pollutants, such as nitrogen oxides (NO_x), CO, and unburned hydrocarbons (UHC). In reality, however, fuel-lean oxidation processes are often substantially affected by the presence of heat-loss phenomena and the severe aerodynamic straining that is imposed upon by the fluid mechanics. In many instances, non-equilibrium effects become important, meaning that within the combustor the oxidation processes cannot be brought locally and/or globally to completion, thus resulting in combustion stability problems and increased UHC and CO emissions.

Enhancing flame stability under such fuel-lean conditions has been commonly accomplished either by preheating the fresh reactants and/or by varying and regulating the fuel composition. Preheating increases flame speed and resistance to extinction, but can, at the same time, increase NO_x emissions, since the overall combustion temperatures are generally higher. The increased flame stability may allow, however, one to use less

fuel, which, in turn, can reduce the overall NO_x emissions. The basic approach proposed for varying and regulating the natural gas composition is through hydrogen addition (Ren et al., 2001). H₂ is more reactive than CH₄ and the other hydrocarbons, which constitute natural gas, and small additions of it can noticeably increase the combustion stability, and also reduce the CO and UHC emission, as well as NO_x, since H₂ can burn at lower temperatures. The basic technical challenge here is the development of an economic H₂-producing technology, since H₂ is not readily available.

Flame stability enhancement can be, alternatively, obtained by varying and regulating the oxidizer (typically air) composition by enriching its O₂ content. Doing so can substantially enhance the overall oxidation process, by affecting the main branching reaction



Reaction (R1) is the main consumption route of O₂ in vigorously burning flames, and the key supplier of O and OH, the two radicals largely responsible for the consumption of the fuel molecules (Westbrook and Dryer, 1981). Increasing the O₂ concentration through O₂ enrichment in the oxidizer results in combustion under thermodynamically favored fuel-lean conditions with enhanced stability, given that the relative significance of heat loss, aerodynamic straining and local/global incomplete combustion as well as NO_x emissions are minimized under such conditions.

Enhancing the combustion temperature

The implementation of OEC in practical high temperature combustors involves two limiting ranges of O₂ concentration. The first is a low region of O₂ molar concentrations, in the range of 21-30%, which is of interest in high-temperature industrial furnaces used

in processing of metals, glass, and ceramics. This low level of O₂-enrichment is economical, and at the same time capable of raising the temperature of the flame as well as its luminosity under fuel-rich conditions, both important for heat transfer purposes. As studies indicate (Qin et al., 2001) even such moderate modifications of the O₂ concentration will affect both the NO_x emissions and the flame shape and topology. The high limit of O₂-enrichment is in the range of 80-95%, which is of interest in oxy-gas combustion. Rigorously speaking, oxy-gas should include only "pure" O₂, but using O₂ of very high purity (>95%) is most definitely an economically prohibitive proposition with current O₂-producing technologies (cryogenic and PSA). Given the particularly high temperatures that result from oxy-gas combustion and the presence of locally and/or globally of N₂ at molar levels of 5-20% in the oxidizer, issues associated with NO_x emissions become important.

For both low and high levels of O₂-enrichment, in addition to NO_x, CO emissions are also an important consideration. While CO emissions for fuel-rich conditions are expected to be a concern from global thermodynamic considerations, for fuel-lean conditions CO emissions may also become a problem due to local extinction events that are associated with weakly-burning flames. While extensive knowledge exists on the mechanisms of NO_x and CO emissions in premixed combustion of natural gas in air, the effect of O₂, prior to the initiation of this study, had not, as yet been systematically addressed. Addition of O₂ can affect the flame thermodynamics and the kinetics of formation for both NO_x and CO, and competing or synergistic mechanisms can affect the corresponding emissions.

Staged Combustion

Staged combustion aims to release the same amount of energy, while simultaneously reducing the amount of NO_x emissions. The 1st stage involves the use of excess fuel, so that the temperatures are low. Thus, the thermal NO_x formation is minimized and at the same time the presence of large amounts of hydrocarbon radicals results in effective NO_x re-burning. In the 2nd stage the balance of the air is added, so that the entire chemical energy of the fuel is recovered. The process is simple, when using air as oxidizer, as it involves only dividing the given amount of air between the two stages. Using OEC, however, offers greater process flexibility. Current approaches, typically, include an air-fired 1st stage, and an O_2 -enriched air fired 2nd stage or alternatively the use of an O_2 -enriched air fired 1st stage and an air-fired 2nd stage, with no clear consensus at present which approach is more effective. In both cases, syn-gas ($\text{CO}+\text{H}_2$) forms from the first stage and must be oxidized in the 2nd stage. The details of syn-gas oxidation are expected to be sensitive to the O_2 composition of the 2nd stage. For example, flame stability, manifested by the flame speed and the resistance to extinction will depend on the O_2 content in the 2nd stage. NO_x will form in both stages, but differences may exist depending on whether O_2 is used in the 1st or the 2nd stage. Current fundamental understanding of such processes is far from satisfactory, and their current implementation is largely based on field empiricism.

Within the context of premixed, oxygen-enriched combustion (preferable mode of operation in practical combustors) a number of technological challenges remain. The issues are subtle, as adding oxygen will simultaneously affect flame propagation, the processes of extinction and ignition, and the pollutant emissions. Such effects can

depend non-monotonically on the oxygen addition. Furthermore, competing effects exist between fuel dilution and oxygen-enrichment effects on the rate of burning, especially for lean burning. In implementing OEC in practice, particularly during staged combustion, the stream of O₂-enriched air is typically directed towards the main fuel/air jet at an angle. Under such conditions, and given the turbulent nature of the flow field, the additional O₂ may be transported either from the upstream or the downstream of the reaction zone. Clearly, the orientation of O₂ entrainment and eventual mixing will play a significant role on the chemical kinetics, as they are of different nature at the upstream and downstream of the reaction zone. Systematic studies on such effect have yet to appear.

As the discussion above has, hopefully, made it clear OEC offers potentially many advantages. In principle, at the limit of using "pure" O₂ the NO_x problem may be entirely eliminated. The technical challenges of such approach, however, directly relate to the efficient and economic production of O₂, as well as to the combustion control under the "unconventional" conditions resulting from the presence of the extra O₂. The challenge of O₂ production must be addressed through the development of novel energetically efficient and economically sound O₂-production processes, as the economics of conventional technologies, like cryogenic oxygen air separation and pressure/temperature swing (PSA/TSA) adsorption methods do not appear promising in the context of energy generation applications. The technological breakthrough here, which is today making OEC a promising reality, is the development of high temperature, oxygen conducting solid oxide membranes. These membranes have been developed recently by two industrial groups. A consortium led, by Praxair and BP/Amoco and another led by Air Products and Eltron Research, Inc. These materials have been studied at the pilot plant

scale (with reported significant success) for catalytic partial oxidation to produce synthesis gas (Dyer et al., 2000). Their use in direct combustion applications, though, in principle, rather straightforward, presents unique technical challenges that must be addressed, before one proceeds to similar-scale, pilot-plant size applications. This was one of the key objectives of this project.

The control of the combustion processes under OEC conditions, particularly in the context of power generation applications (flame stability enhancement and re-burning), still remains a challenge. This can be best met when the propagation, extinction, and pollutant formation processes are understood at the flamelet level, as the knowledge on the combustion of CH₄/air mixtures is of no help in predicting the OEC characteristics. Fundamental knowledge at the flamelet level can be subsequently used to scale the combustion characteristics of large-scale combustors. This fundamental knowledge, furthermore, must be extended to higher pressures above atmospheric, as pressure has an important effect on the oxidation kinetics, which is not always monotonic or "obvious". For example, as a result of the competition between the main branching reaction (R1) and the main termination reaction



the effect of O₂ enrichment on the burning rate may not be as beneficial at elevated pressures during lean-burning, since under such conditions (R1) may be favored relatively to (R2). Such issues need to be resolved experimentally and theoretically.

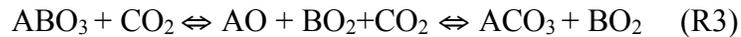
This project has involved combustion studies of model laminar flames established in the stagnation and counter-flow configurations that can be modeled exactly, and are, in

addition, archetypes that closely describe the local flame behavior in realistic turbulent flow-fields, as those encountered in gas turbines and furnaces. Key flame properties have been measured, including flame speeds, extinction conditions, temperature structures, and stable species and NO_x concentration profiles. The measurements have been taken utilizing a variety of techniques, currently existing in our labs, including Laser Doppler Velocimetry (LDV), thermocouple technology, micro-probe sampling and Molecular Beam Mass Spectrometry together with GC/MS for stable species measurements, and micro-probe sampling, and Chemiluminescence for NO_x species measurements. The experiments have been numerically simulated using exact models that included the use of detailed chemical kinetics, molecular transport, and thermal radiation. The studies have provided important insight on the effect of O_2 -enrichment on the flame dynamics and structure and pollutant emissions. The main research conclusion is that indeed OEC of NG can, under lean-burning conditions, result in more stable combustion with lower NO_x emissions for the same flame temperatures.

1.3 Mixed Solid Oxide Oxygen Conducting Membranes

Dense, mixed solid oxide oxygen conducting membranes have both good oxygen and electronic conductivity. In recent years these membranes have been utilized in membrane reactors during the partial oxidation of light hydrocarbons, and for the oxygen enrichment of air. These applications require that the structure of the mixed oxide membrane is mechanically and chemically stable under the operating conditions. As a result, a number of investigations in recent years have focused on the study of phase stability characteristics of these membranes.

Kreuer (1997), for example, has discussed the stability of proton conductors in the presence of CO₂. Typically these materials have an ABO₃ perovskite-type structure and can potentially react with CO₂ according to the following reaction:



Kreuer (1997) studied two commonly utilized materials (BaCeO₃ and SrCeO₃), and reported that the stability of BaCeO₃ material is higher than that of SrCeO₃. In a subsequent study Kreuer (1999) studied YBaZrO₃, and reported that it has good thermodynamic phase stability together with high proton conductivity.

Van Doorn *et al.* (1998) have studied a La_{0.3}Sr_{0.7}CoO_{3-d} perovskite membrane that was exposed at 900 °C to separate streams of air and inert gas on opposite sides of the membrane; they report that a phase separation occurs at the oxygen-lean side of the membrane. After the membrane had operated for over 500 h at temperatures between 900 ~ 1000 °C, its surface characteristics were studied, and it was observed that the side of membrane in contact with the oxygen-lean feed side had degraded more severely than the opposite side. Surprisingly, however, the oxygen permeation flux remained unaltered during the time span of the measurements. Nevertheless, Van Doorn *et al.* (1998) note that these phenomena deserve more attention, as phase de-mixing could lead to membrane deterioration, loss of performance, or even mechanical failure.

Shao and co-workers (2000) prepared SrCo_{0.8}Fe_{0.2}O_{3-d} (SCFO) and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d} (BSCFO) membranes using a combined citrate and EDTA complex method. The BSCFO membranes showed stability characteristics at lower oxygen partial pressures, which were superior to those of the SCFO membranes. A high

oxygen permeability was observed for the BSCFO membrane at 950 °C, and minor amounts of CO₂ and water vapor in the air seemed to have less of an effect on the permeation flux of the BSCFO than that of SCFO. No phase transition was found at oxygen partial pressures in the range of 1 ~ 10⁻⁵ atm at 850 °C. The BSCFO membranes were operated stably for more than 1000 h at 850 °C.

Ahmad-Khanlou *et al.* (2000) studied by XRD and SEM the effect of Ga content on the crystallinity, sintering behavior, microstructure and conductivity of a La_{0.8}Sr_{0.2}Ga_{0.9+x}Mg_{0.1}O_{3-d} (-0.02 < x < 0.04) perovskite. They report that small changes in the Ga content manifest themselves in the type of crystalline phases identified, the sintering behavior, the morphology, and electrical conductivity. Therefore, it is difficult to attain stable properties for perovskite materials with the composition La_{0.8}Sr_{0.2}Ga_{0.9}Mg_{0.1}O_{3-d}. A related perovskite material La_{0.5}Sr_{0.5}Ga_{0.2}Fe_{0.8}O_{3-d} (LSFGO) was shown to be unstable (Ming, 1999), and decompose at 860 °C under a simulated syngas environment, with a corresponding oxygen partial pressure of about 10⁻¹⁷ atm.

Another challenge in the preparation of mixed solid oxide membranes is to attain sufficiently high oxygen and electronic conductivities. One idea is to prepare asymmetric membranes, in which a thin dense layer of the material is deposited on a porous structure of the same material (in order to avoid thermal mismatch). Van der Haar and Verweij (2000), for example, prepared porous La_{1-x}Sr_xCoO_{3-d} (x=0.7, 0.5 and 0.2) substrates as supports for the preparation of such asymmetric mixed ionic-electronic conducting perovskite membranes. After isostatic pressing (400 MPa) followed by sintering (at 1100 °C), the supports were 30% porous with a mean pore diameter of 1 μm. A method was described to improve the surface morphology of the supports, which involves applying

(after polishing) a coating with the same composition as the support. The gas permeability of these porous supports was fairly low, however.

A class of perovskite materials that have attracted attention in recent years are LaSrCoFeO perovskites. Petric and coworkers (2000) have evaluated these materials for solid oxide fuel cells and gas separation membranes. They report that perovskite compounds $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-d}$ with $0.2 < x < 0.4$ and $y < 0.5$ seem to have very attractive transport properties as gas separation membranes.

Xu and co-workers (Xu *et al.* 2000; Li *et al.* 2000a, 2000b; Jin *et al.* 2000) studied $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ (LSCF), $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ (LBCF), $\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_{3-d}$ (SCF) and ZrO_2 doped $\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_{3-d}$ (SCFZ) perovskite membranes. They found that LBCF and SCFZ are the more stable materials.

Ma and Balachandran (1997) have studied the properties of $\text{SrFeCo}_{0.5}\text{O}_x$ perovskites and have shown that $\text{SrFeCo}_{0.5}\text{O}_x$ exhibits not only high electronic and oxygen ionic conductivities, but also structural stability in both oxidizing and reducing atmospheres. This material is technologically important for uses in high-temperature electrochemical applications, since it has good stability at high temperature. Balachandran and coworkers report the use of these perovskite materials in membrane reactors for the conversion of methane into syngas. The reactor with the $\text{SrFeCo}_{0.5}\text{O}_y$ membrane run stably for more than 1000 h at 850 °C (Balachandran 1995,1998; Lu *et al.* 2000).

There has been no published study, prior to this one, that we are aware of, that has focused on the application of perovskite membrane materials to OEC. In this project we have studied the application of dense $\text{SrCo}_{0.5}\text{FeO}_3$ membranes in a membrane reactor for this system. The $\text{SrCo}_{0.5}\text{FeO}_3$ membranes, showed good stability, even when two sides of the membrane were at very low oxygen partial pressure.

2 Project Objectives

The project goal was to evaluate the technical feasibility and environmental implications of a novel technology involving an OTM/OEC hybrid concept within the context of power/energy generation. The technology envisions O₂ production to take place in a oxygen transport membranes. To accomplish the goal the project addressed the following four objectives:

- 1) Determination of the technical feasibility of coupling oxygen transport membranes (OTM) with oxygen enhanced combustion (OEC). Determination of the stability characteristics of membranes in the OEC environment.
- 2) Determination of the combustion stability of the OTM/OEC hybrid concept.
- 3) Determination of the pollutant formation characteristics, with particular emphasis on NO_x emissions. Quantification of the technology potential for attaining NO_x emissions in the single ppm digit range.
- 4) Determination of the potential of the OTM/OEC technology for improving gas turbine efficiency, and its potential for achieving efficiencies in excess of 35 %.

3 Project Approach

3.1 Preparation of the SrCo_{0.5}FeO₃ Membrane Disks

The membranes utilized in this work were made from a ceramic SrCo_{0.5}FeO₃ powder prepared by the solid state reaction route (Balachandran *et al.*, 1995). SrCO₃ (99% pure, from Aldrich), Fe₂O₃ (99.945% pure, from Johnson Matthey) and

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% pure, from Mallinckrodt Baker Inc) were precisely weighed, so that after the solid state reaction they would create a compound with a molar composition of that of $\text{SrCo}_{0.5}\text{FeO}_x$. They were then mixed by ball-milling with zirconia balls for 20 h. The mixtures were calcined at 1123 K for 16 h in air. The calcined powder mixture was ground in a mortar and pestle and was again ball-milled. The powder was then mixed in a mortar, with polyvinyl alcohol (PVA) solution added as a binder, and was pressed isostatically at 150 Mpa for 1 min to form a disk (33 mm in diameter, and 2 mm thick). After drying, the green sample was placed in an alumina sample holder, and inserted in a programmable high temperature furnace. The temperature of the sample was raised at 1 K/min, until the temperature reached 773 K; after that the temperature was raised again at a rate of 2 K/min, until a pre-selected temperature was reached. The disk is calcined at this temperature, typically, for 2~5 h. The crystal structure of the resulting $\text{SrCo}_{0.5}\text{FeO}_3$ membrane disk was determined by X-ray powder diffractometry (XRD) on a Rikago diffractometer with $\text{CuK}\alpha$ radiation.

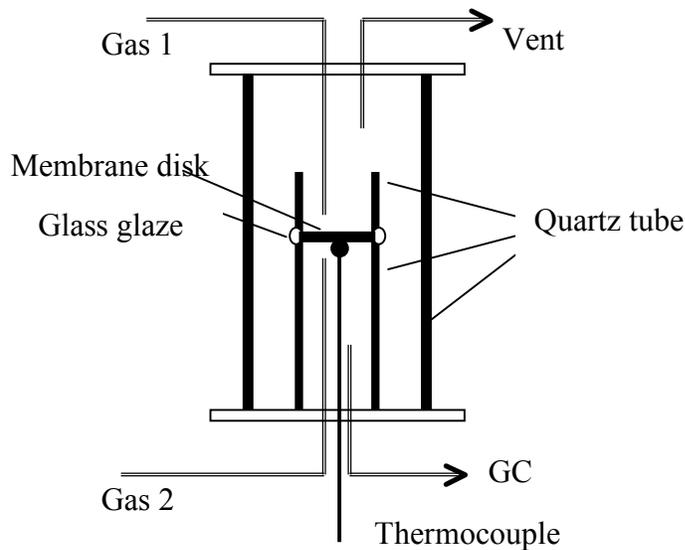


Fig. 1 Schematic of the experimental apparatus.

The experimental membrane reactor apparatus is shown in Fig. 1. For the oxygen permeation measurements, air was fed to the top chamber (gas 1), and helium or a mixture of helium and methane was fed to the bottom chamber (gas 2). For the OEC membrane experiments air was fed into the bottom chamber, while methane mixed with argon was fed to the top membrane reactor chamber. The content of oxygen or carbon dioxide was determined with a Varian 3400 gas chromatograph using a carbon molecular sieve packed column and helium as the carrier gas. Oxygen permeates through solid oxide membrane; carbon dioxide and unreacted CH₄ remain in the reactor chamber and are analyzed by gas chromatography

3.2 Combustion Experiments

The combustion experiments were carried out using the stagnation-flow experimental configuration, in which planar flames are established between a nozzle and a variable temperature plate (in lieu of a flat membrane) that acts as the stagnation plane (Egolfopoulos *et al.* 1997). Measurements were conducted along the stagnation streamline, and included the determination of flow velocities, stable species concentrations, and NO_x. The flow velocities were determined through Laser Doppler Velocimetry (LDV). A typical velocity profile has a near-zero gradient at the nozzle exit and gradually develops an increasing slope, which reaches its maximum just before the minimum velocity point, where heating starts. This maximum velocity gradient in the hydrodynamic zone is defined as the imposed aerodynamic stretch, K , and the minimum velocity as a reference upstream flame speed, $S_{u,ref}$, as proposed by Law and coworkers

(Law 1988). To determine the laminar flame speed, S_u^0 for a given mixture, $S_{u,ref}$ is plotted with respect to K , and S_u^0 is found by linearly extrapolating to $K = 0$.

Stable combustion requires a balance between fluid mechanics, heat and mass transfer, and chemical kinetics. When this balance is perturbed flame extinction occurs, characterized by a sharp reduction in the chemical activity and heat release; local and global extinction events in a combustor can lead to lower combustion efficiency and increased pollutant emissions. By increasing the nozzle exit velocity, K increases and the flame is pushed towards the stagnation plane, and at a critical value, K_{ext} , extinction is eventually obtained (Law 1988). In the present study, the extinction strain rates, K_{ext} , were also determined.

The NO_x concentrations were determined by quartz microprobe sampling connected to a Chemiluminescence $NO-NO_2-NO_x$ analyzer. In order to avoid surface catalytic effects, the probe was water-cooled when sampling the high-temperature combustion products. The accuracy of the measured NO_x concentrations is estimated to be within 5%. All measurements were conducted at atmospheric pressures, with a burner nozzle 22 mm in diameter, and a separation distance between the nozzle exit and the stagnation plate of 16 mm.

3.3 Combustion Simulations

The laminar flame speeds were also calculated using the one-dimensional Premix code of Kee *et al.* (1985). The numerical simulation of the counter-flow configuration for the determination of the extinction strain rates, the concentration flame structures, and NO_x were conducted by using the one-dimensional stagnation flow code (Egolfopoulos *et*

al. 1996). The code integrates the steady-state mass, momentum, energy, and species conservation equations along the stagnation streamline in a finite domain. In both codes radiative heat transfer from CH₄, H₂O, CO₂, and CO was included (Law *et al.* 1992). The codes were linked to the Chemkin-II (Kee *et al.* 1989) and Transport (Kee *et al.* 1983) subroutine libraries. The GRI 3.0 mechanism (Bowman *et al.* 1999) was used for the description of the C₁- and C₂-hydrocarbon oxidation and NO_x kinetics.

4 Project Outcomes

4.1 Membrane Reactor Experiments

The X-ray diffraction pattern of the SrCo_{0.5}FeO₃ membranes used in our experiments has been presented elsewhere (Ren *et al.*, 2003). It is similar to the one reported by Balachandran *et al.* (1995, 1998), which proves that the materials prepared by our group are the same (in terms of their XRD signature) with the materials reported in the literature. Figure 2 depicts the O₂ permeation fluxes of two different SrCo_{0.5}FeO₃ membrane disks prepared by our group, measured using He as a sweep gas and for the same temperature of 1173 K. Oxygen fluxes at different temperatures for one of these membranes (taken between the period of 142 to 152 h in the experiments of Fig. 2) are shown in Fig 3. The oxygen flux values shown in Figs. 2 and 3 are similar to those

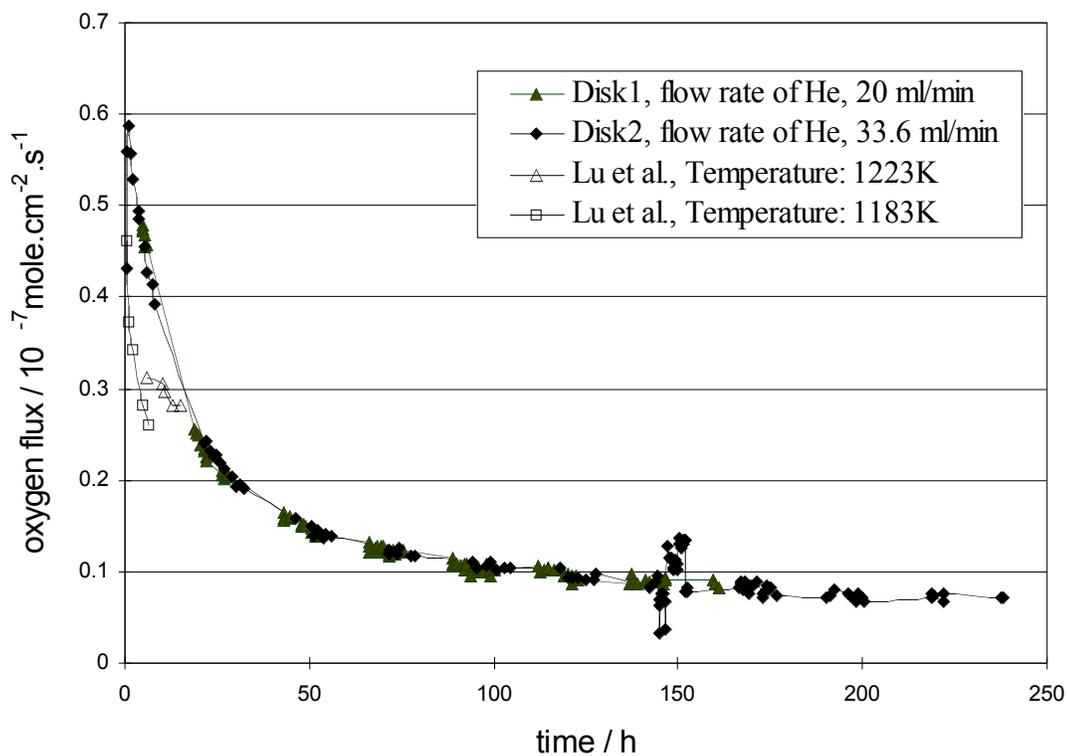


Fig. 2 The oxygen flux of two SrCo_{0.5}FeO₃ membrane disks (temperature, 1173K). Shown also on the figure are data by Lu *et al.*(2000)

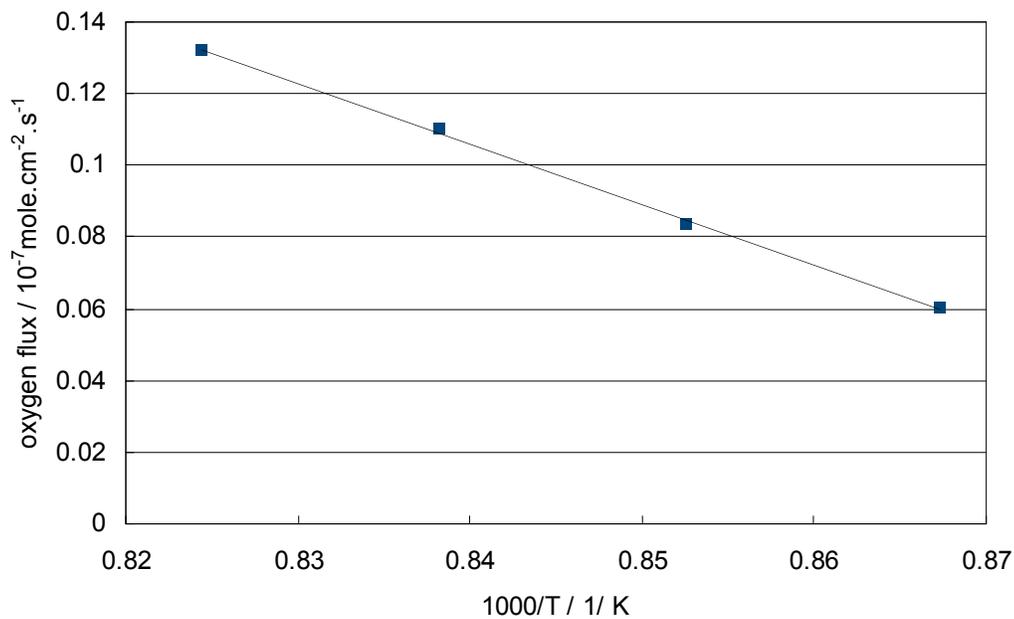


Fig. 3 The oxygen flux at different temperatures

reported by Lu *et al* (2000) (for comparison, some of these data are also shown in Fig. 2). It should be noted from Fig. 2, that we are able to prepare membranes with highly reproducible properties, when measured under inert conditions. In order to test the oxygen permeation under OEC relevant reactive conditions, experiments have also been carried out in which He was replaced with a reactive sweep consisting of a mixture of CH₄ in He. The oxygen fluxes of a SrCo_{0.5}FeO₃ membrane disk under OEC reactive conditions are shown in Fig. 4. The O₂ fluxes under OEC conditions are significantly higher (50-60 times on the average) than the fluxes measured in the presence of the He sweep gas (their values are similar to those reported by Balachandran *et al.* (1995)). Interesting to note is also that the disks behave qualitatively differently under inert and OEC conditions. While under inert conditions the flux declines significantly for a period of hours before it levels off, the opposite is true for the experiments under reactive conditions. Shown also in Fig. 4 is the oxygen flux due to air leaking either through pinholes and microcracks in the membrane or through the glass seals. This leak flux is calculated based on the amount of nitrogen that one observes in the sweep (permeate) chamber. For the data shown in Fig. 4 the oxygen flux, due to the air leak, corresponds to less than 7% of the oxygen flux through the membrane. With the time on stream increasing, however, the air leak increases, indicative potentially of additional pinholes and microcracks developing through the membrane and or/the seals. For the membrane of Fig. 4, for example, after 10 days continuously on stream the oxygen flux due to the air leak rose to about 20% of the flux through the membrane itself. Improving the thermal and mechanical stability of membrane materials and seals in these types of OEC reactive environments remains a key challenge of the commercial application of the membranes in OEC.

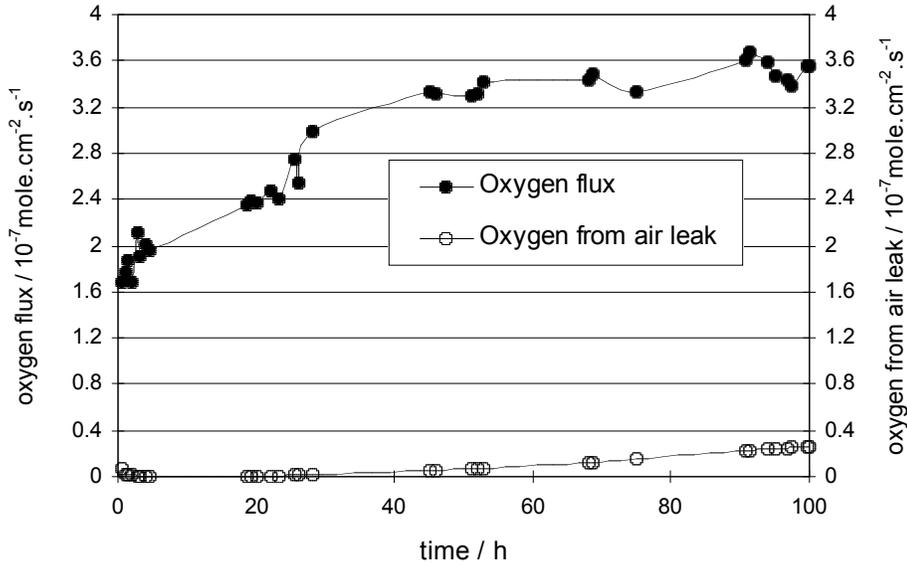


Fig. 4 The oxygen flux of a $\text{SrCo}_{0.5}\text{FeO}_3$ membrane disk with a reactive sweep (Air flow, 108 ml/min; sweep gas consists of He 10 ml/min + CH_4 10 ml/min; temperature 1173K).

4.2 Combustion Stability

The effect of oxygen enrichment on laminar flames speeds, S_u^0 , was first numerically determined for $\phi_{\text{init}}=0.60, 0.65, 0.70, 0.75, 0.80,$ and 0.85 and the results are shown in Fig. 5. Note that X_{O_2} stands for the mole of fraction of O_2 in the oxidizer, while ϕ_{init} represents the initial equivalence ratio of a mixture in which O_2 was added. Initially, X_{O_2} was chosen to be greater than 21%, which corresponds to the O_2 mole fraction in normal air. It was realized that while for most values of ϕ_{init} , S_u^0 decreases with X_{O_2} , it was found that for some ϕ_{init} values, S_u^0 exhibits a maximum with respect to X_{O_2} . For the $\phi_{\text{init}}=0.85$ case, for example, a maximum value was identified for $X_{\text{O}_2}=23.7\%$. This motivated the extension of the simulations for values $X_{\text{O}_2}<21\%$, and the complete picture

of the simulations is shown in Fig. 6. A maximum of S_u^0 is identified now for all ϕ_{init} values, with this maximum occurring at lower X_{O_2} values, as ϕ_{init} is reduced. This non-monotonic behavior predicted by the simulations, was confirmed experimentally by measuring flame speeds for the $\phi_{init} = 0.85$ and 0.70 cases. The results are also shown in Fig. 6. Indeed, maximum values of S_u^0 are experimentally reproduced along both ϕ_{init} curves, providing, thus, confidence to the numerical predictions.

The variation of X_{O_2} while keeping X_{N_2}/X_{CH_4} constant, results in variation of ϕ as mentioned earlier. In Fig. 6 the higher values of X_{O_2} correspond to lean mixtures ($\phi < 1$), while the lower values of X_{O_2} correspond to rich mixtures ($\phi > 1$); note that the response of flames with $\phi < 1$ and $\phi > 1$ is controlled by different kinetics. The calculated

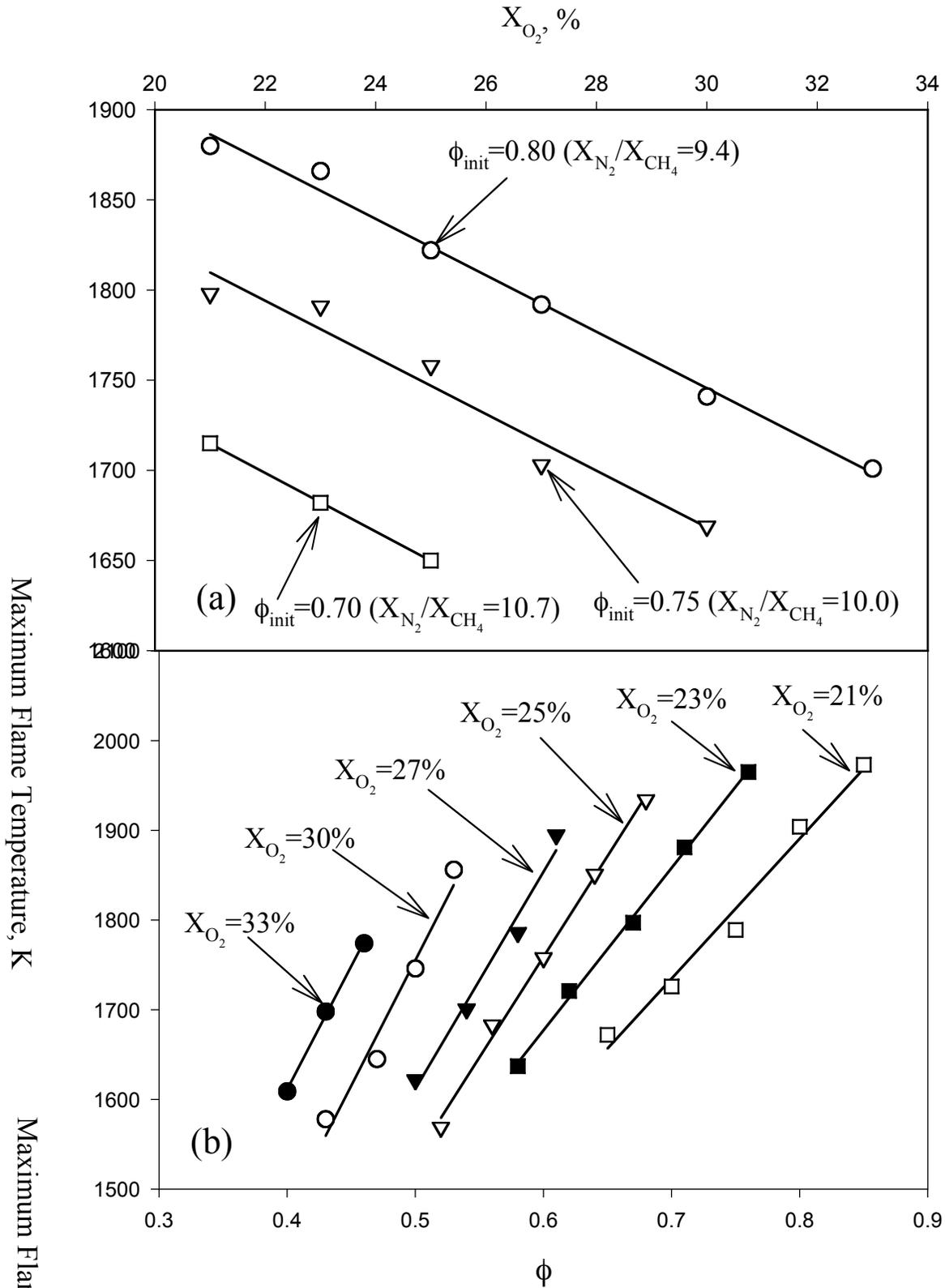


Fig. 5 Experimentally determined T_{max} as functions of (a) X_{O_2} and for various ϕ_{init} 's, (b) ϕ and for various X_{O_2} 's.

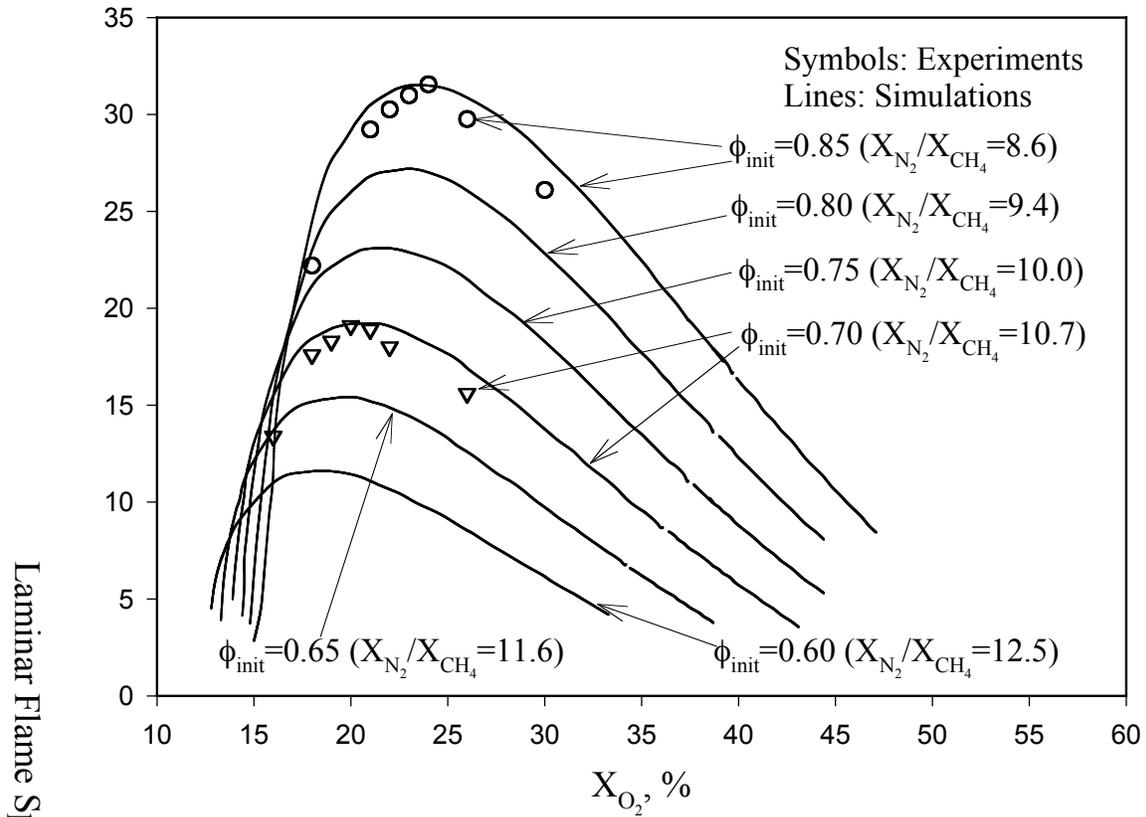


Fig. 6 Experimentally and numerically determined S_u^0 as function of X_{O_2} and for various ϕ_{init} 's.

S_u^0 's of Fig. 6 are shown in Fig. 7a as functions of ϕ , and for the various ϕ_{init} 's. All curves appear to have a maximum between $\phi=0.70$ and 0.75 . Figure 7b depicts the corresponding T_{max} variation as function of ϕ , and for various ϕ_{init} 's. Similarly to S_u^0 , all T_{max} curves exhibit a maximum value. Interestingly, for all cases reported in Fig. 7b, the T_{max} appears to occur between $\phi=0.90$ and 0.95 .

The observations of Figs. 7a and 7b bring up an interesting point. While T_{\max} peaks around $\phi=0.90$ to 0.95 , S_u^O peaks around $\phi=0.70$ to 0.75 . This means that for a fixed X_{N_2}/X_{CH_4} , adding O_2 to a flame with ϕ between 0.9 and 0.75 , on one hand reduces T_{\max} and on the other increases S_u^O . The physical explanation of this observation, is based on the response of the main branching reaction (1) to the simultaneous X_{O_2} enhancement and T_{\max} reduction, as flame propagation is particularly sensitive to the rate of (R1). The variation of the maximum rate of (R1) with ϕ is shown in Fig. 8a, for various ϕ_{init} values, and maximum values are observed to occur between $\phi=0.70$ to 0.75 , similarly to the S_u^O . The rate of (1) depends on both temperature and O_2 concentration. While, the reduction of T_{\max} by adding O_2 and reducing ϕ from 0.90 to 0.75 tends to reduce the rate of (R1), the effect of O_2 concentration increase dominates the temperature effect and as a result, the rate of (1) increases, thus increasing S_u^O . Figure 8b also depicts the variation of the maximum rate of the main termination reaction



that has a negative effect on propagation, and its rate can be also affected by the O_2 addition. By comparing the maximum rates of (R1) in Fig. 8a and (R2) in Fig. 8b, it is apparent that the rate of (R2) is one order of magnitude lower compared to (R1) in the $0.70 < \phi < 0.75$ region, where S_u^O peaks. Furthermore, (R2) appears to peak in the $0.60 < \phi < 0.65$ region, which is reasonable as it is a three-body reaction and it is favored at

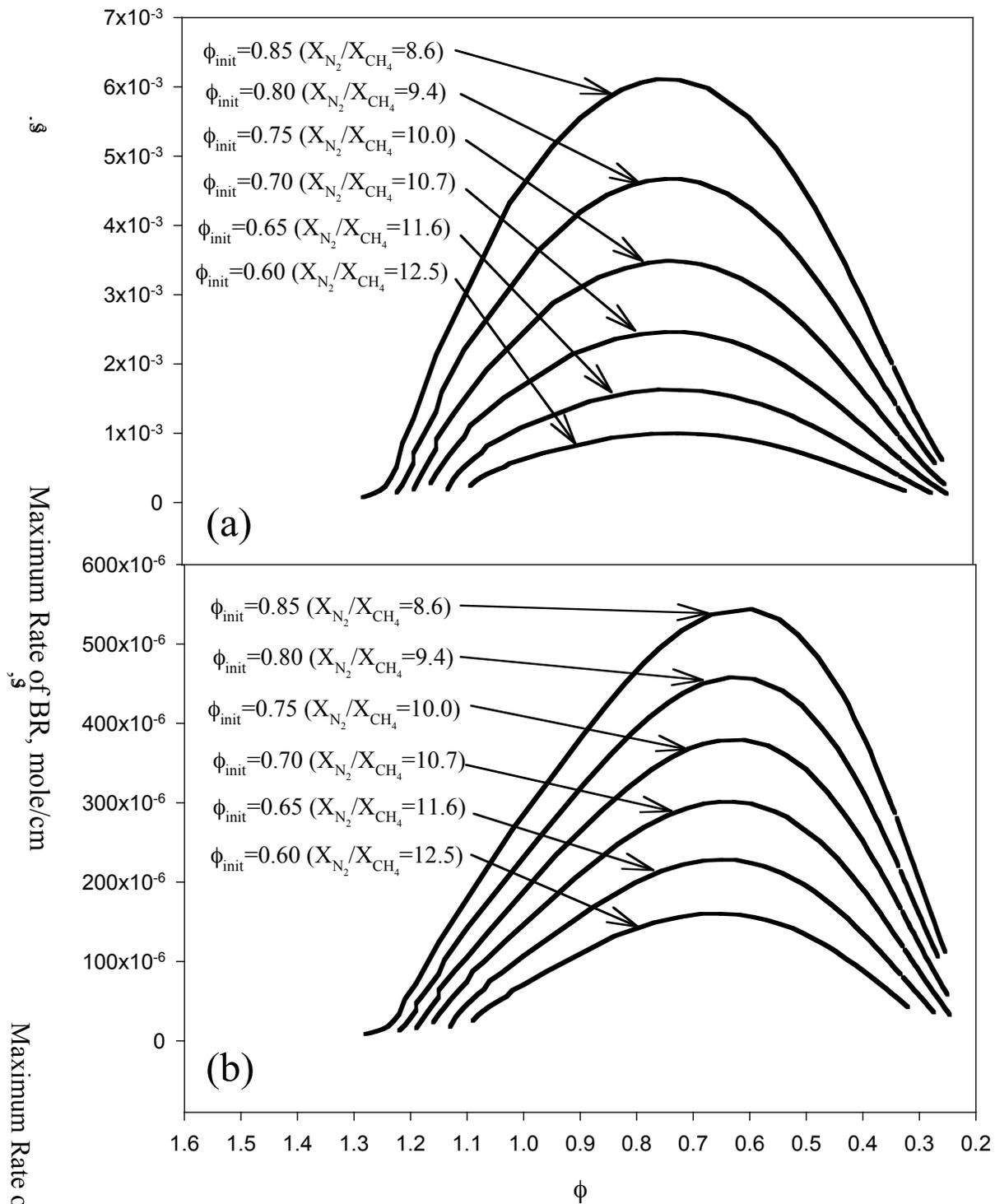


Fig. 8 Numerically determined maximum rates for (a) $H+O_2 \rightarrow OH+O$ branching reaction and (b) $H+ O_2+M \rightarrow HO_2+M$ termination reaction, as functions of ϕ and for various ϕ_{init} 's.

lower temperatures compared to (R1). Thus (R2) has no significant effect on S_u^0 around its maximum value.

The results of Figs. 6-8 also reveal a substantial reduction of T_{max} with X_{O_2} , in accord with the experimental results of Fig. 5. At the same time, and especially for the leaner mixtures (i.e. lower values of ϕ_{init}), it was found that the corresponding reduction of S_u^0 is more gradual compared to T_{max} because of the competing effects of T_{max} reduction and O_2 concentration enhancement, as discussed earlier. This has an important implication for the stability of lean combustion. One observes that for the same flame temperature (i.e. T_{max}) more stable combustion conditions are achieved by increasing X_{O_2} , as S_u^0 , a measure of flame stability, increases. Given that the purpose of lean combustion is the reduction of NO_x emissions, it is also of interest to note that this can be achieved more effectively with higher X_{O_2} , as stable combustion can be established at lower T_{max} .

It should be also noted, that while the results of Figs. 6-8 corresponding to $X_{O_2} < 21\%$ are of fundamental interest, they are also of practical importance. While O_2 addition in a real combustor is in general expected to result in $X_{O_2} > 21\%$, conditions of $X_{O_2} < 21\%$ may, in fact, be locally encountered. For example, in a turbulent flow field, and under conditions of poor mixing (intentional or unintentional), the combustion products of rich-fuel pockets can mix with fresh reactants, and dilute thus the O_2 content; the products of rich combustion contain N_2 but no O_2 .

The enhancement of flame stability through O_2 addition was further assessed, by calculating the effect of the addition on the fundamental flammability limits. The ability of a mixture to sustain stable combustion increases as its S_u^0 increases, and as its

resistance to extinction increases. For lean combustion, the resistance to extinction increases as the value of the lean flammability limit decreases, extending thus the flammable range. Lean flammability limits were determined by obtaining a turning-point response in the ϕ domain for mixtures with fixed values of X_{O_2} , and the results are shown in Fig. 9. The substantial reduction of the limit value of ϕ as X_{O_2} increases is apparent, supporting the beneficial effect of O_2 addition on flame stability.

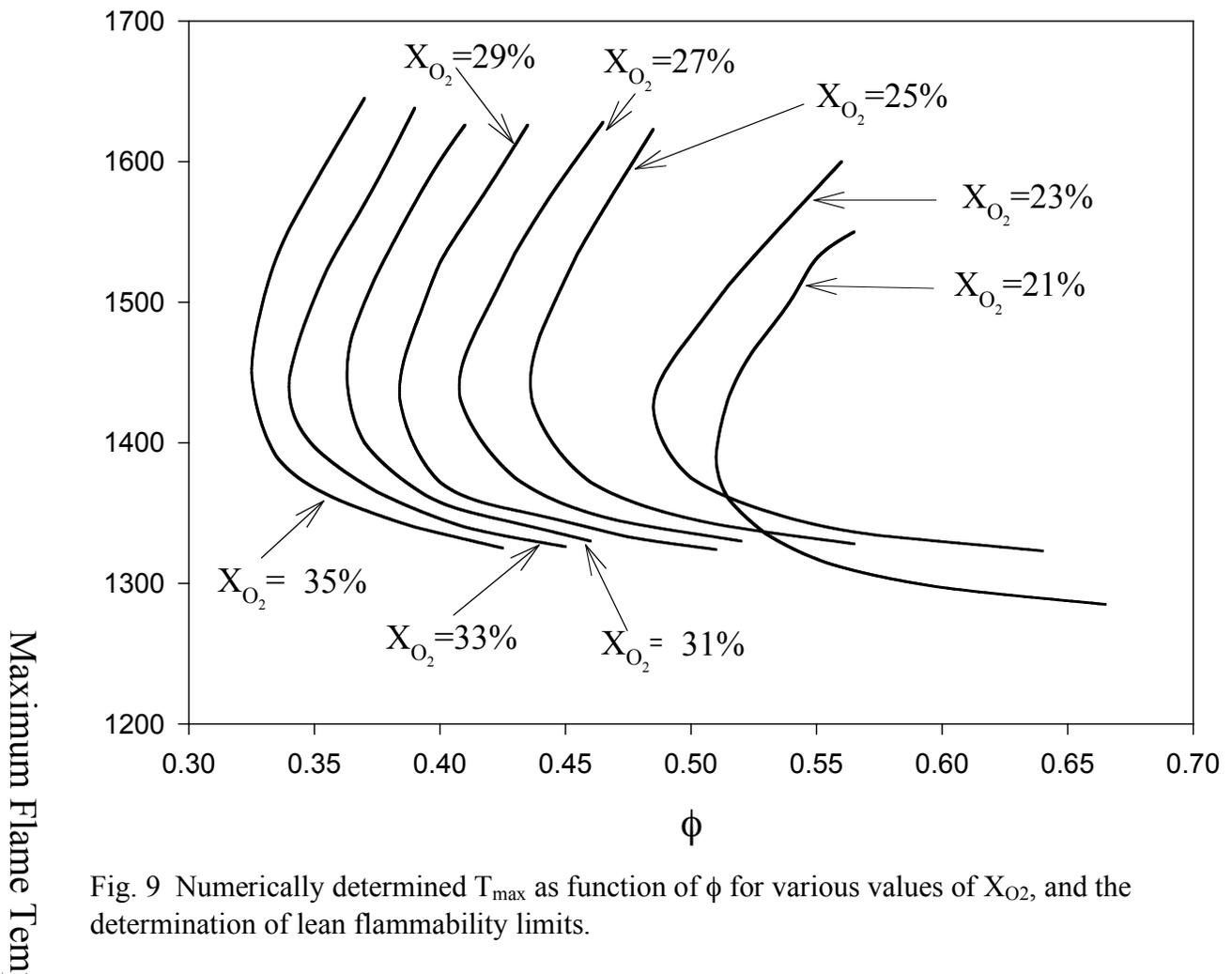


Fig. 9 Numerically determined T_{max} as function of ϕ for various values of X_{O_2} , and the determination of lean flammability limits.

4.3 Pollutant Formation Characteristics

The effect of the O_2 enrichment on NO_x formation was studied experimentally and numerically by varying X_{O_2} , similarly to the flame propagation studies. Both experiments and simulations included the determination of total NO_x (i.e. NO and NO_2) concentration profiles in the stagnation flow configuration, and the identification of the maximum NO_x value, $(X_{NO_x})_{max}$, in ppm observed, similarly to the T_{max} determination.

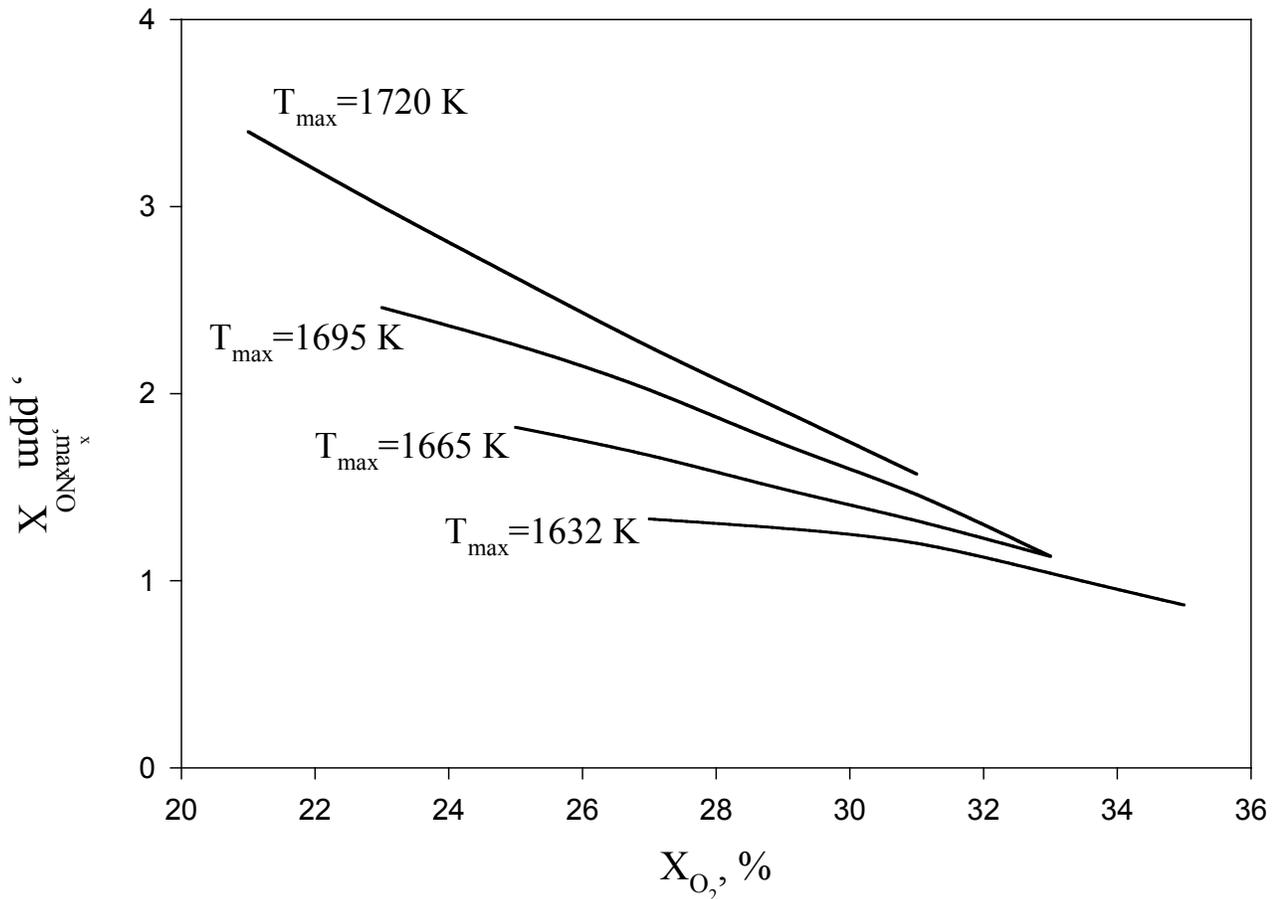


Fig. 10 Numerically determined $X_{NO_x,max}$ as function of X_{O_2} and T_{max} .

Figure 10 depicts the variation of the numerically determined $(X_{\text{NO}_x})_{\text{max}}$ with X_{O_2} , for flames with same T_{max} . The results indicate that for the same X_{O_2} (thus, same N_2 concentration), flames with higher T_{max} produce more NO_x , as expected. Furthermore, for the same T_{max} , the flames with higher X_{O_2} produce less NO_x , which is a result of the reduced N_2 concentration. The effect of O_2 enrichment on reducing NO_x for flames of fixed T_{max} appears to be more efficient, when O_2 is added to flames with higher T_{max} . This is physically reasonable, as NO_x production for these lean flames is of thermal nature, and the hotter flames have higher propensity in producing NO_x . Thus, the reduction of N_2 concentration (as X_{O_2} increases), will have a greater impact in reducing NO_x production in high T_{max} flames, as compared to low T_{max} flames in which the NO_x production rate is already low.

Figure 11 depicts the variation of $(X_{\text{NO}_x})_{\text{max}}$ with X_{O_2} , as numerically determined for a wide range of X_{O_2} values and for $\phi_{\text{init}}=0.60, 0.65, 0.70, 0.75, 0.80,$ and 0.85 . Interestingly, a double peak behavior is observed for the $\phi_{\text{init}}=0.75, 0.80,$ and 0.85 cases. For the $\phi_{\text{init}}=0.60, 0.65,$ and 0.70 cases, a monotonic behavior is observed, as these flames are characterized by higher $X_{\text{N}_2}/X_{\text{CH}_4}$ values, and the reduction of X_{O_2} weakens them readily to the point of extinction. For $X_{\text{O}_2}>21\%$ and for all ϕ_{init} 's, it is seen that for the same X_{O_2} , flames with higher ϕ_{init} produce more NO_x , and this is a result of the higher flame temperature. Furthermore, $(X_{\text{NO}_x})_{\text{max}}$ is substantially reduced as X_{O_2} increases for fixed $X_{\text{N}_2}/X_{\text{CH}_4}$. Physically, this reduction is caused by the synergistic effect of the reduced flame temperature and the reduced N_2 concentration as X_{O_2} increases.

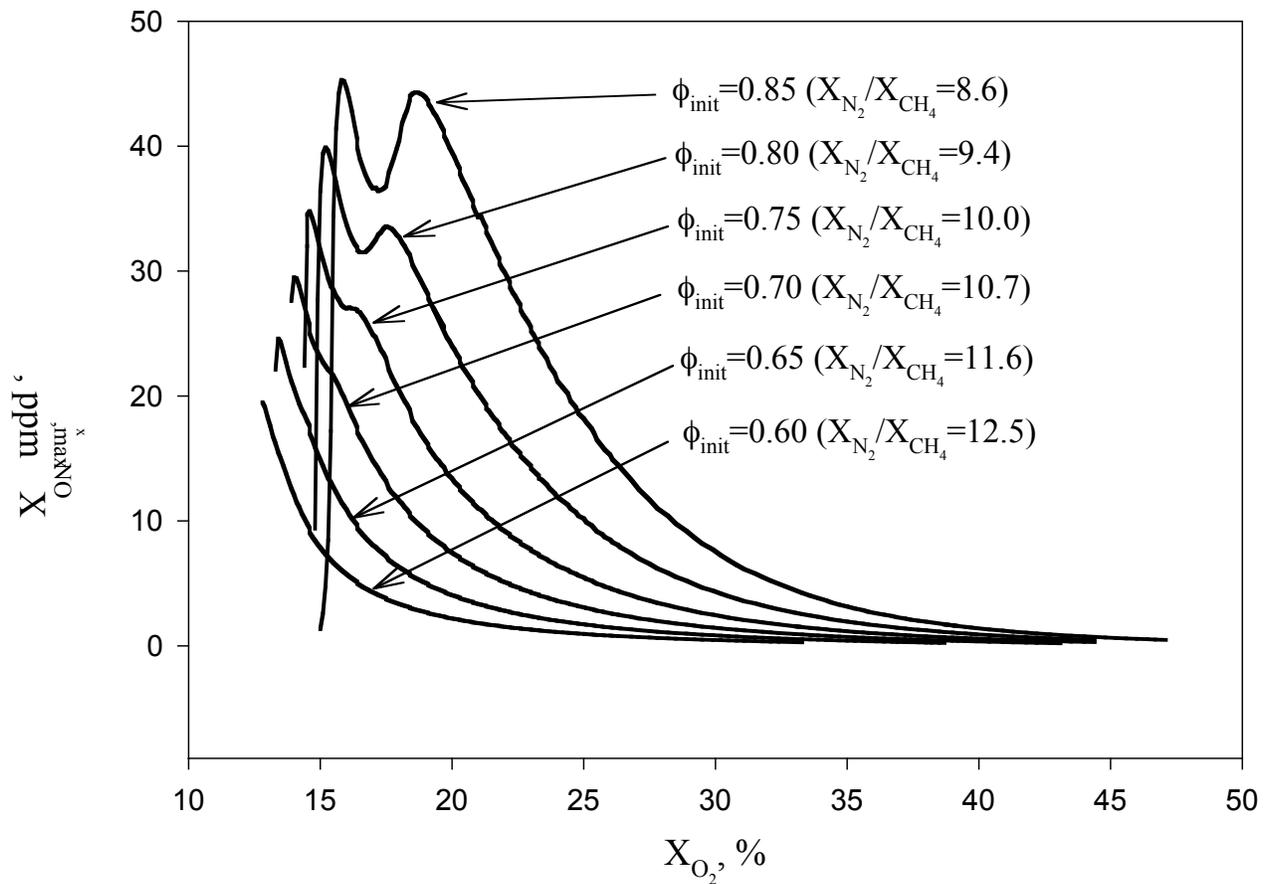


Fig. 11 Numerically determined $X_{NOx,max}$ as function of X_{O_2} and for various ϕ_{init} 's.

The non-monotonic behavior shown in Fig. 11 was experimentally investigated by measuring $(X_{NOx})_{max}$ for the $\phi_{init}=0.85$ case, and for various X_{O_2} values. The experimental results along with the numerical simulations for the $\phi_{init}=0.85$ case are shown in Fig. 12, and indeed a maximum of $(X_{NOx})_{max}$ is observed at the same X_{O_2} value derived from the simulations. This provides confidence to the NO_x predictions of the model. The second maximum could not be reproduced as flames are ultra-rich and can not be stabilized. Figure 12 also depicts the variation of T_{max} with X_{O_2} , and it can be seen that the peak of $(X_{NOx})_{max}$ at about $X_{O_2}=19\%$ nearly coincides with the peak of T_{max} , which explains the existence of the first maximum point, as NO_x production is sensitive

to temperature. The second maximum point, however, at about $X_{O_2}=16\%$ exists in a region in which T_{max} is decreasing as X_{O_2} decreases.

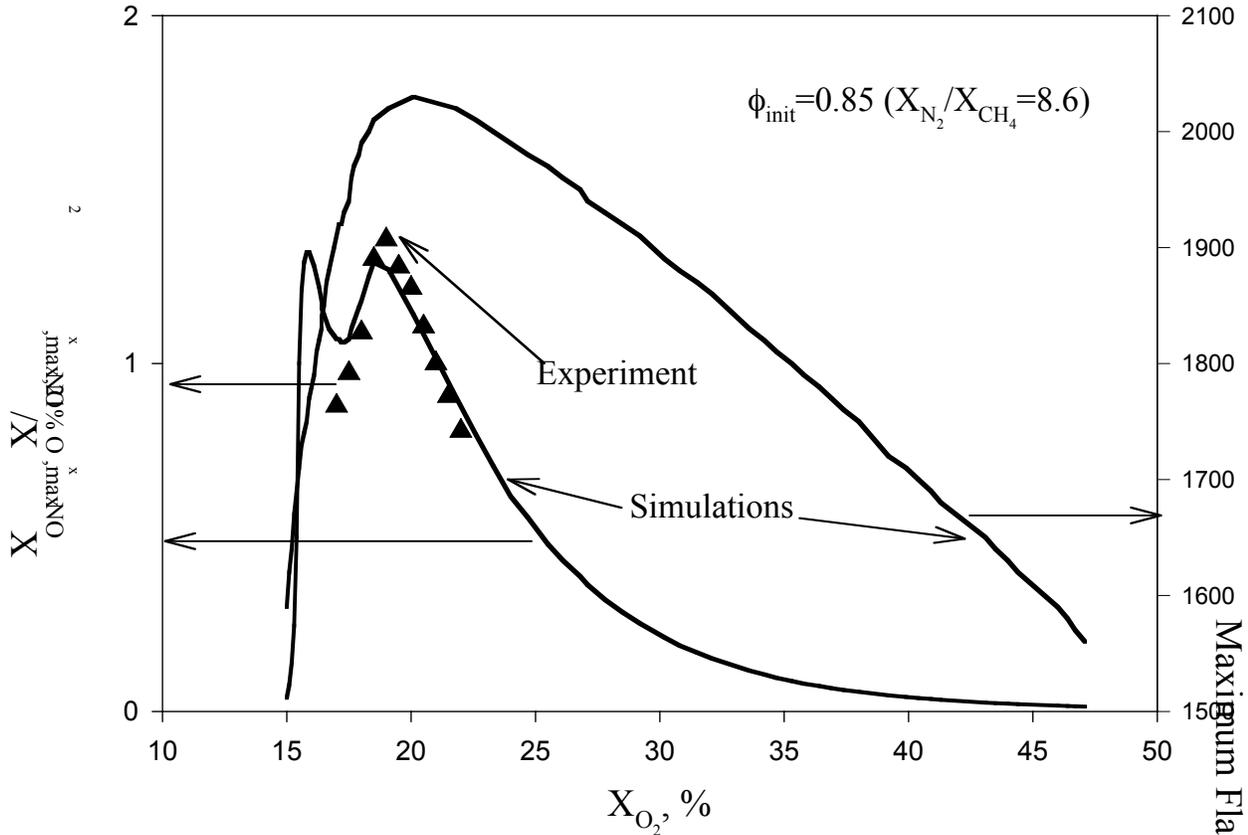
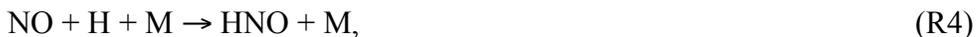


Fig. 12 Experimentally and numerically determined $X_{NO_x,max}$ (scaled by values obtained at $X_{O_2}=21\%$), and numerically determined T_{max} as functions of X_{O_2} and for $\phi_{init}=0.85$.

In order to explain the mechanisms of the second $(X_{NO_x})_{max}$ peak at about $X_{O_2}=16\%$, the main NO production and consumption kinetic steps were identified through integrated species production/consumption path analyses. Results revealed that for values of X_{O_2} around 19% (where the first peak of $(X_{NO_x})_{max}$ is observed) the NO is largely consumed through reaction:



while it is equally produced through reactions:



From this production/consumption mechanism, it is apparent that the concentration of HNO depends on the progress of all three reactions. Furthermore, reactions (R4) and (R5) form a closed loop as the main product of (R4) becomes the main reactant of (R5) and vice versa. Addition of (R4) and (R5) results in $\text{H} + \text{H} \rightarrow \text{H}_2$, suggesting that NO and HNO can play a catalytic role in such radical recombination.

The analysis revealed that as X_{O_2} is reduced approaching 16%, while (R4) remains the main consumption step, the importance of consumption step is (R5) enhanced. The role of (R6) in producing NO was found to rapidly diminish as the flames become more rich (lower X_{O_2}), and the OH concentration is reduced at a rate that is faster compared to the reduction of H. Reactions (R4) and (R5) have a similar activation energy, and a constant ratio between the two rates was found for a wide range of X_{O_2} . Given that the concentration of HNO is controlled by the combined effect of (R4), (R5), and (R6), its value is expected to depend on the relative rates of these reactions. It was found that the concentration of HNO increases as X_{O_2} decreases and reaches a maximum at about $X_{\text{O}_2}=16\%$, which is also the X_{O_2} value at which the $(X_{\text{NO}_x})_{\text{max}}$ peaks, as shown in Fig. 13. This is a result of the reduction of the rate of (R6). The maximum HNO concentration results in a maximum for $(X_{\text{NO}_x})_{\text{max}}$. The subsequent reduction of $(X_{\text{NO}_x})_{\text{max}}$ as X_{O_2}

further decreases, is a result of the reduction of the overall chemical activity and radical production as a rich flammability limit is approached.

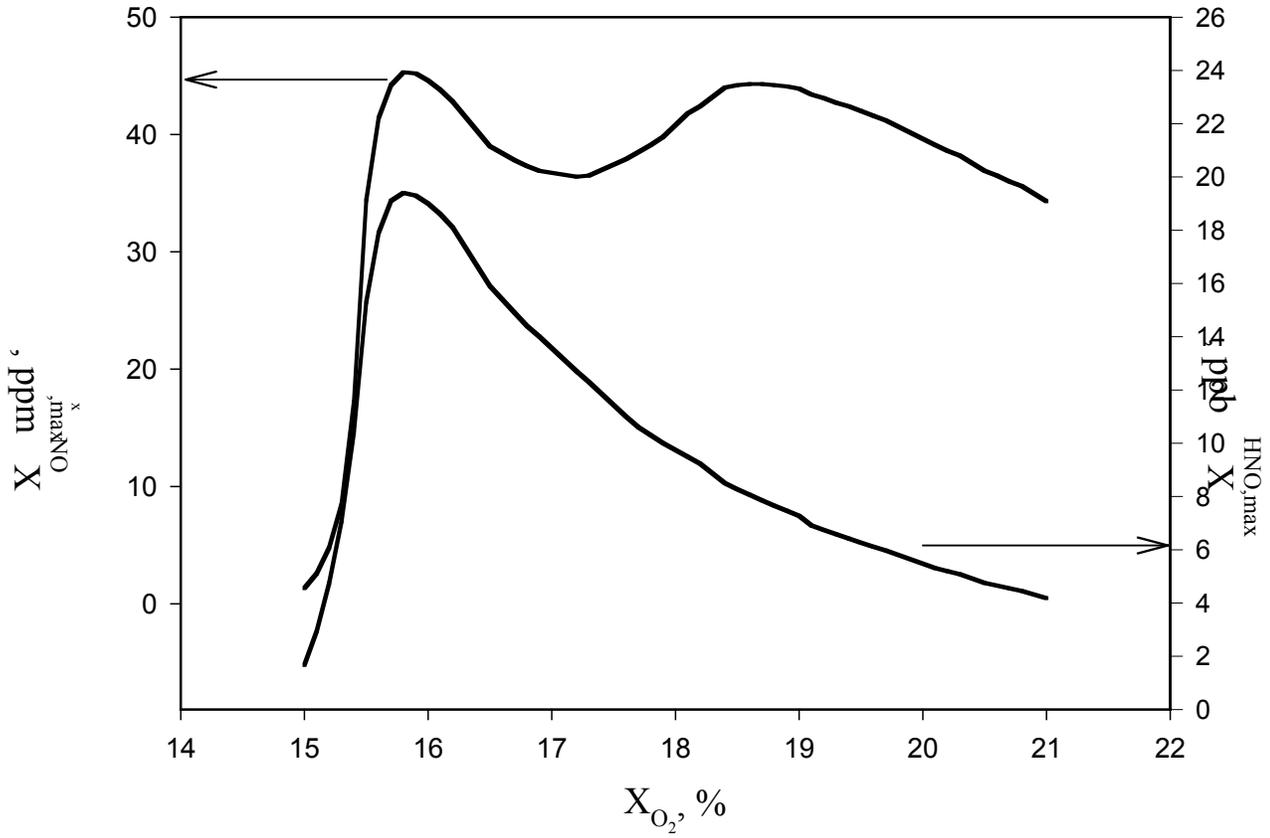


Fig. 13 Numerically determined maximum concentrations of NO and HNO as functions of X_{O_2} and for $\phi_{init}=0.85$.

4.4 Oxygen-Lancing for Fuel-lean Flames

Experiments were first carried out to validate the kinetic models with experimental data on flame thermal structures and pollutant concentrations. Figure 14 depicts experimental (points) and simulated (lines) results on the effect of X_{O_2} on the flame thermal structure for a flame with $\phi = 0.7$, $u_{\text{exit}} = 50$ cm/s, distance between nozzles, $L = 1.1$ cm (simulating the proximity of membrane to the flame), and for $X_{O_2} = 21\%$ (no O_2 enrichment), $X_{O_2} = 40\%$, and $X_{O_2} = 100\%$, the latter corresponding to a perfect O_2 permselective membrane (in this and all remaining figures the CH_4 /air mixture is supplied from the left and the O_2 enriched air or pure O_2 from the right of the domain). The experimental data are closely predicted for all cases. Figure 15 depicts the NO_x (the sum of NO and NO_2) concentration profiles for the same three flames. There is a satisfactory agreement between theory and experiments upstream of the flame, but a systematic ($\sim 10\%$) over-prediction of the measured maximum NO_x molar concentration, $(X_{NO_x})_{\text{max}}$, just downstream of the flame region. The agreements in Figs. 14 and 15, and similar agreements observed previously (Qin *et al.*, 2000; Ren *et al.*, 2001, 2002), provide confidence in the kinetic models, and in extending the simulations to additional conditions relevant to O_2 lancing.

Figure 16 depicts results for a perfect membrane (pure O_2) and indicates the effect of the temperature of the O_2 stream exiting the membrane on flame temperature (Fig. 16a) and NO_x emissions (Fig. 16b). Note that, for the fuel-lean flame ($\phi=0.85$, CH_4 /air flame), increasing this temperature results in an increase of NO_x emissions with simultaneous increase of the maximum flame temperature. The increase of NO_x emissions is due to the

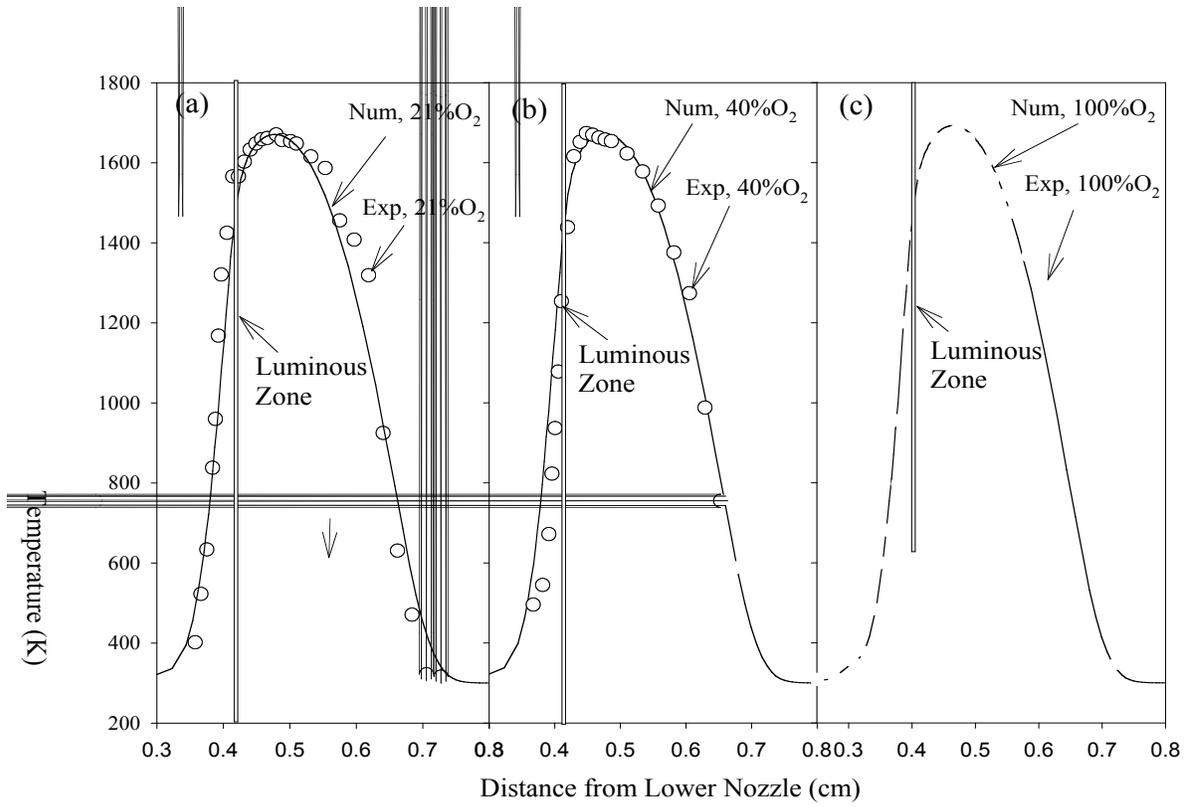


Fig. 14 Temperature profiles. ($\phi=0.7$, $u_{\text{exit}}=50$ cm/s, $L=1.1$ cm)

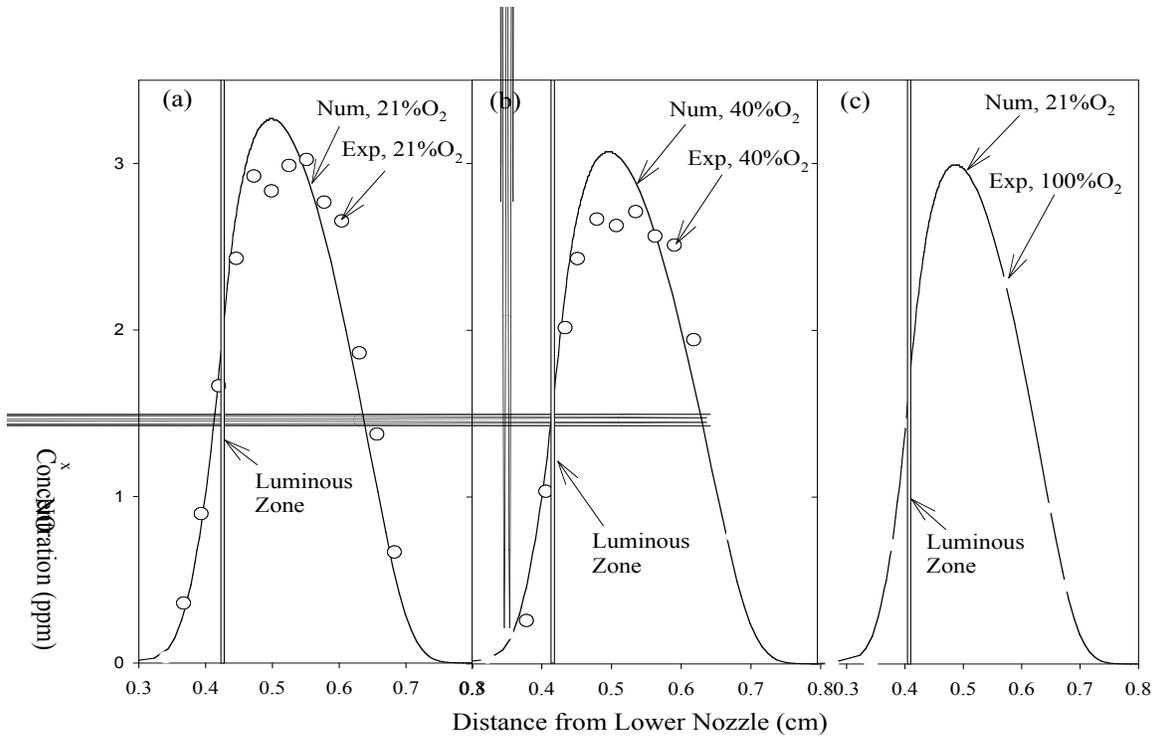


Fig. 15 NO_x Profiles ($\phi=0.7$, $u_{\text{exit}}=50$ cm/s, $L=1.1$ cm).

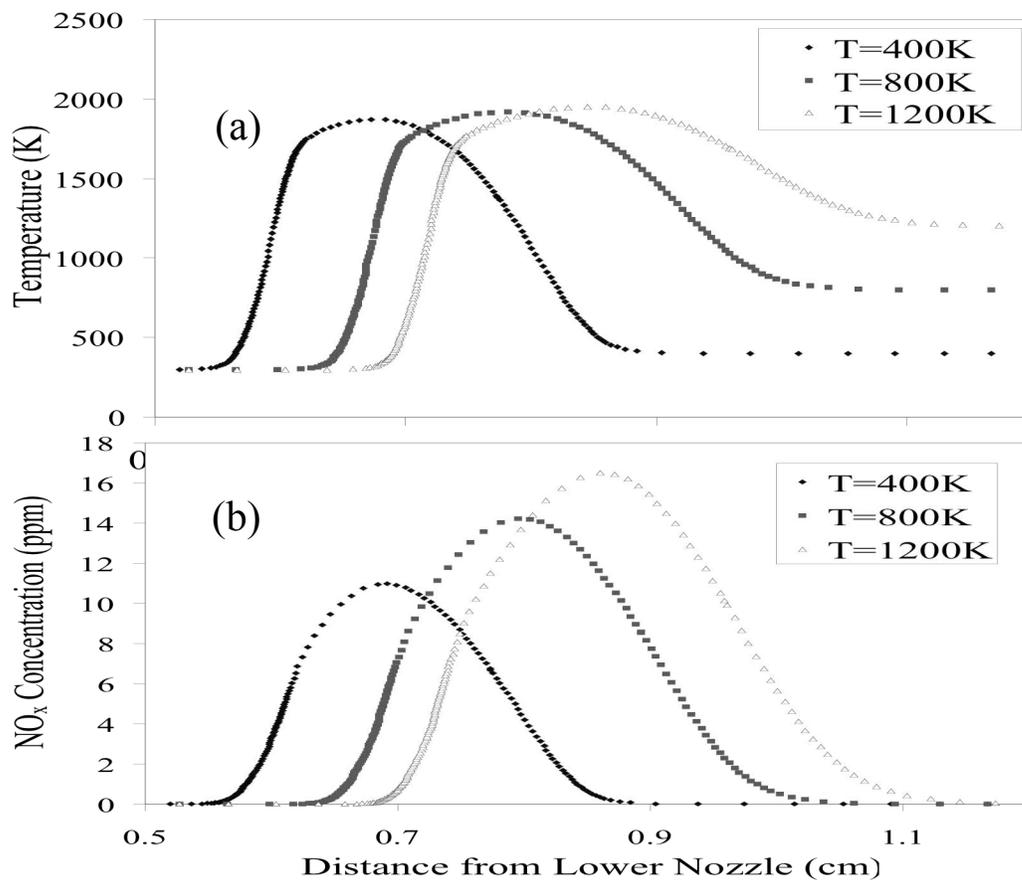


Fig. 16 Effect of downstream temperature (a) Flame temperature, (b) NO_x profiles ($\phi=0.85$, $u_{\text{exit}}=150$ cm/s, $L=1.4$ cm, $X_{\text{O}_2}=100\%$).

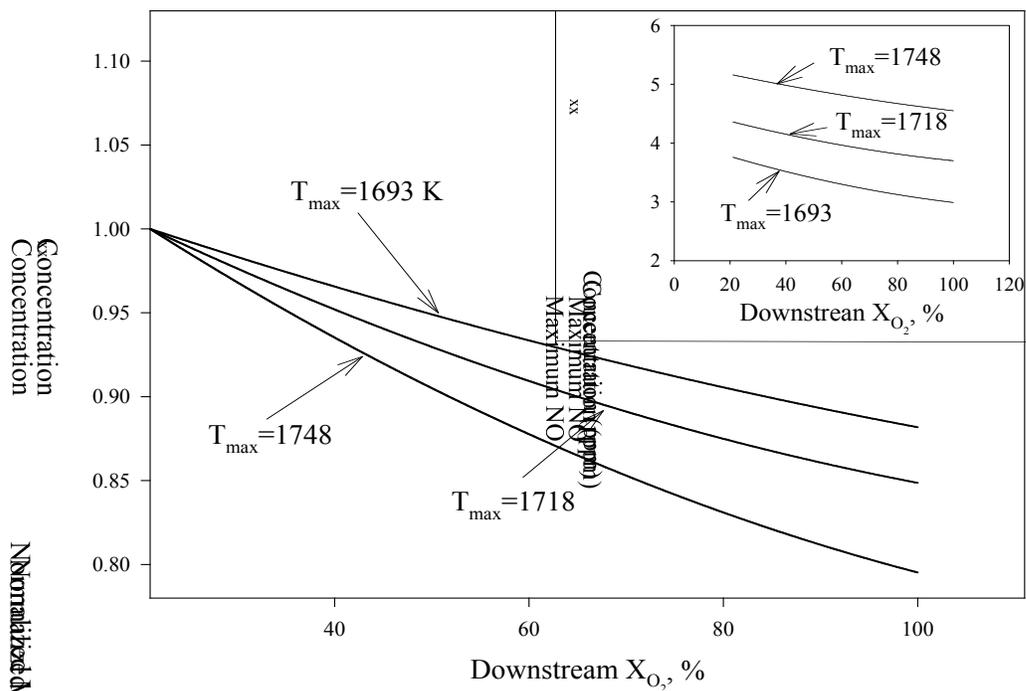


Fig. 17 Calculated maximum NO_x concentration as function of downstream X_{O₂} and T_{max} ($\phi\sim 0.7$, $u_{\text{exit}}=50$ cm/s, $L=1.1$ cm).

increase of the thermal NO_x formation rate, which is strongly temperature dependent. Figure 17 depicts the predicted $(X_{\text{NO}_x})_{\text{max}}$ as a function of X_{O_2} and of the maximum flame temperature, T_{max} , for given u_{exit} and L . The reported values are normalized by the value corresponding to the $X_{\text{O}_2} = 21\%$ (no O_2 enrichment); the actual NO_x values are shown in the insert figure. Results are shown along constant T_{max} lines, first because T_{max} is a measure of the energy/power output of each flame (an important performance criterion in practical combustors), and second because by fixing the T_{max} the temperature effect on NO_x formation is suppressed, so that the kinetic effects from O_2 enrichment are isolated and independently studied. Experimentally, T_{max} is maintained constant as X_{O_2} increases by lowering the ϕ of the CH_4/air stream. The results of Fig. 17 indicate that for a fixed T_{max} , there is a reduction of $(X_{\text{NO}_x})_{\text{max}}$ as X_{O_2} increases (more apparent for flames with higher T_{max}). For example, for $T_{\text{max}} = 1748 \text{ K}$, $(X_{\text{NO}_x})_{\text{max}}$ is reduced by about 20% as X_{O_2} varies from 21% to 100%. As expected, the results shown in the insert indicate the detrimental effect of T_{max} on $(X_{\text{NO}_x})_{\text{max}}$. Analysis indicates (Ren, 2002) that there are two mechanisms responsible for the behavior in Fig. 17. First, the reduction of the N_2 concentration in the postflame region, as X_{O_2} increases, directly affects the rate of NO_x formation. Second, as X_{O_2} increases ϕ must decrease in order for T_{max} to remain constant, and the CH concentration decreases; this diminishes the contribution of the prompt mechanism by reducing the forward rate of its initiation reaction $\text{N}_2 + \text{CH} \rightarrow \text{HCN} + \text{N}$. The contribution of the prompt mechanism is greater for the flame with $T_{\text{max}} = 1748 \text{ K}$ and $X_{\text{O}_2} = 21\%$, as it has a ϕ greater than the flames with lower T_{max} ; ϕ reduction for the more stoichiometric flames with higher T_{max} has a more profound effect in reducing the contribution of the prompt mechanism, as compared to the less stoichiometric flames with lower T_{max} values.

4.5 Oxygen Lancing for Fuel-rich Flames

The effect of O_2 enrichment on fuel-rich flames was investigated for a $\phi = 1.4$ flame with $L = 1.4$ cm, $u_{\text{exit}} = 150$ cm/s, and three levels of enrichment, i.e. $X_{O_2} = 21\%$, 40% , and 100% . Figure 18a depicts experimental (points) and predicted (lines) CO and CO_2 profiles. Figure 18b depicts NO_x and temperature profiles. Note that as X_{O_2} increases the maximum concentration of CO, $(X_{CO})_{\text{max}}$, $(X_{NO_x})_{\text{max}}$, and T_{max} all increase. The position of the maximum also shifts towards the lower nozzle as X_{O_2} increases, suggesting that the flame speed increases. This is because a non-premixed flame is established downstream of the rich premixed flame; the reactants for this flame are the unreacted CO and H_2 supplied from the premixed flame, and O_2 supplied from downstream. The extra heat released from the non-premixed flame, causes a further increase in temperature; as a result, the premixed flame becomes super-adiabatic, and its flame speed increases. Analysis reveals that as X_{O_2} increases the O_2 content within the reaction zone of the premixed flame also increases, as some of the O_2 leaks through the non-premixed flame. This makes the premixed flame more stoichiometric and further contributes to the flame speed increase, but to a lesser extent than the aforementioned heat transfer mechanism. The observed increase of $(X_{CO})_{\text{max}}$ with X_{O_2} is also a result of the changes in temperature and stoichiometry within the reaction zone, thus resulting in higher CO concentrations through the enhancement of the $CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO$ chain sequence, with the CH_3 conversion to CH_2O being particularly sensitive to the O concentration.

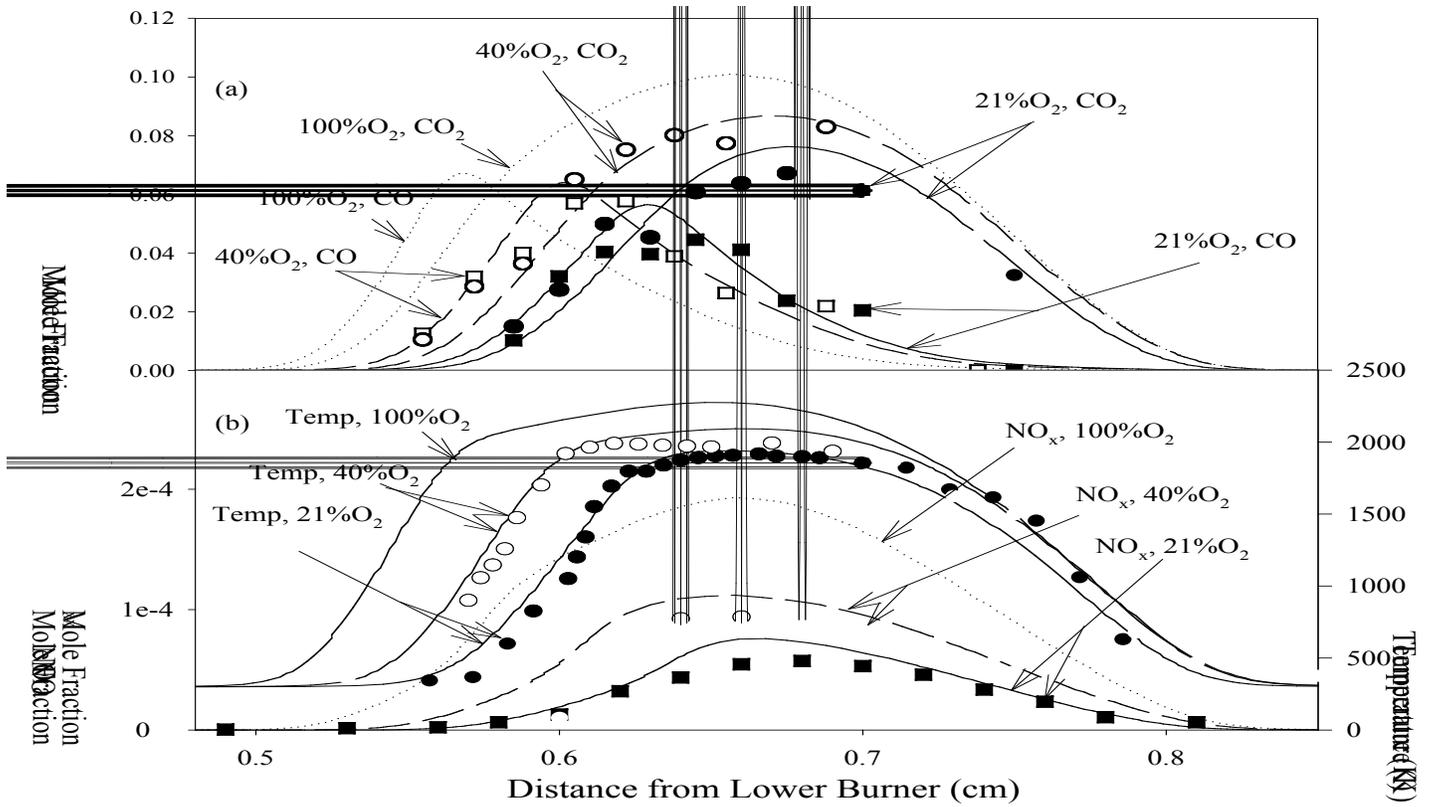


Fig. 18 (a) CO/CO₂, (b) NO_x and temperature profiles ($\phi=1.45$, $u_{\text{exit}}=150$ cm/s, $L=1.4$ cm, $X_{\text{O}_2}=21, 40$, and 100%).

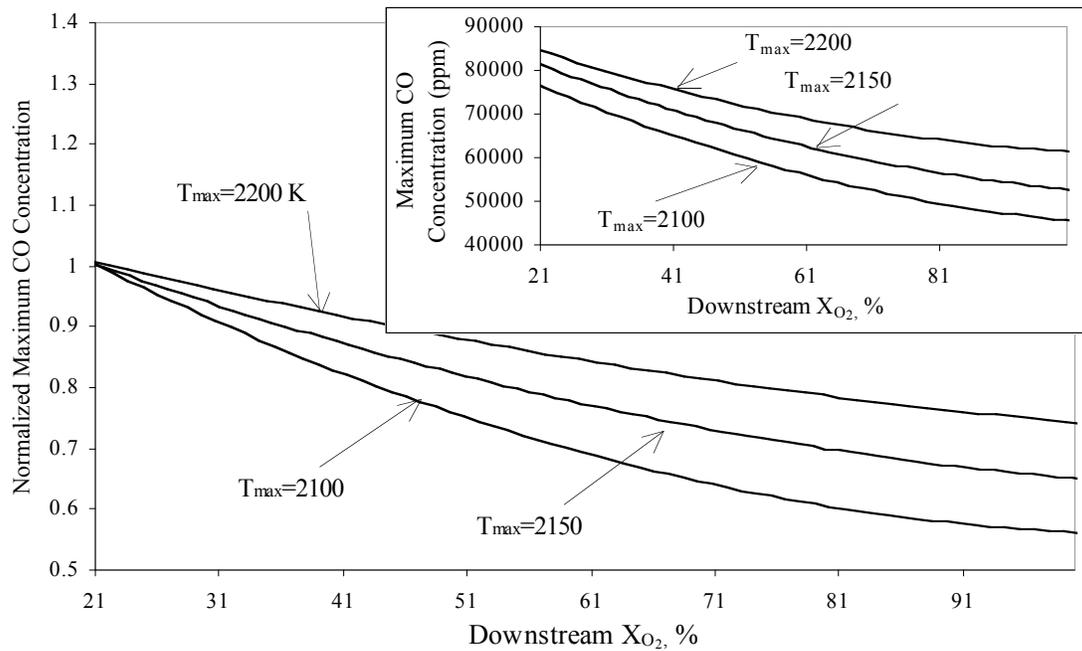


Fig. 19 Calculated maximum CO concentration as function of downstream X_{O_2} and T_{max} ($\phi>1$, $u_{\text{exit}}=150$ cm/s, $L=1.4$ cm).

$(X_{\text{CO}})_{\text{max}}$ and $(X_{\text{NO}_x})_{\text{max}}$ were also calculated as function of X_{O_2} for the same T_{max} ; the results are shown in Figs. 19 and 20. Note in these figures the beneficial effect of O_2 enrichment in reducing the CO/NO_x emissions for flames with same T_{max} , especially for the lower T_{max} . For the case of $T_{\text{max}} = 2100 \text{ K}$, for example, $(X_{\text{CO}})_{\text{max}}$ is reduced by about 40%, while $(X_{\text{NO}_x})_{\text{max}}$ decreases by about 70 % as X_{O_2} increases from 21% to 100%. The explanation for the reduction of $(X_{\text{CO}})_{\text{max}}$ and $(X_{\text{NO}_x})_{\text{max}}$ as X_{O_2} increases for fuel-rich flames is as follows. As reported in the discussion of Fig. 17, for fuel-lean flames, T_{max} is kept constant as X_{O_2} increases by decreasing ϕ , i.e. by making the flame *less stoichiometric*. This is because by increasing X_{O_2} the local O_2 concentration within the main reaction zone increases; our observations show that this increases the temperature, so that a constant T_{max} can only be maintained by reducing ϕ . In Figs. 19 and 20, T_{max} is maintained constant by also decreasing ϕ as X_{O_2} increases, which in this case makes the flame *more stoichiometric*. To understand this, one must note that for $\phi > 1$ flames CO and H_2 are present in the postflame region and react with the O_2 supplied from downstream to form a non-premixed flame. The temperature of the non-premixed flame is the highest value, T_{max} , throughout the domain, and close to one expected for a stoichiometric flame corresponding to the concentrations of the reactants, i.e. CO , H_2 , and O_2 ; for a given ϕ , as X_{O_2} increases T_{max} increases coincident with the increase of O_2 supply from downstream. Our analysis shows that in order for T_{max} to be kept constant, ϕ must decrease, i.e. the premixed flame must become *more stoichiometric*, which reduces the supply of CO and H_2 downstream of the premixed flame. As ϕ is reduced, lower values of $(X_{\text{CO}})_{\text{max}}$ are realized, as there is enough OH to effectively consume CO through $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$. For larger ϕ , the CO is only partially oxidized and its concentration is significantly enhanced in the post-flame region.

The reduction of $(X_{\text{NOx}})_{\text{max}}$ with X_{O_2} is also a consequence of the accompanying reduction of ϕ . It is known (Samaniego *et al.*, 1998; Sung & Law, 1998; Drake & Blint, 1991) that as ϕ increases the relative importance of the prompt NO over the thermal NO mechanism increases. Analysis has revealed that the N_2 destruction rate through the thermal NO mechanism ($\text{N}_2 + \text{O} \rightarrow \text{N} + \text{NO}$) peaks at the location of T_{max} as it should; note that such location coincides with the location of the non-premixed flame, as noted earlier. On the other hand, the N_2 destruction rate through the prompt mechanism ($\text{N}_2 + \text{CH} \rightarrow \text{HCN} + \text{N}$) is found to peak within the reaction zone of the premixed flame at the exact location where the CH concentration also peaks. The N_2 destruction rate through the thermal mechanism was found to be similar for the various flames of different ϕ 's but of the same T_{max} . This is reasonable, as the thermal mechanism is mostly sensitive to the maximum flame temperature. In contrast, the rate of N_2 destruction through the prompt mechanism is found to decrease as ϕ decreases, given that there is more O_2 available to eventually oxidize CH so that the prompt mechanism initiation reaction with N_2 is not favored. As a result, as X_{O_2} increases and ϕ decreases, to keep the T_{max} constant, $(X_{\text{NOx}})_{\text{max}}$ decreases. The fact that the reduction of $(X_{\text{CO}})_{\text{max}}$ and $(X_{\text{NOx}})_{\text{max}}$ is more profound for the lower values of T_{max} can be also explained by realizing that a more effective reduction of ϕ must be imposed as X_{O_2} increases to keep the T_{max} constant at a lower value as compared to a higher value. This is because reducing ϕ more rapidly results in a more effective reduction of the postflame CO and H_2 concentrations that tend to increase T_{max} .

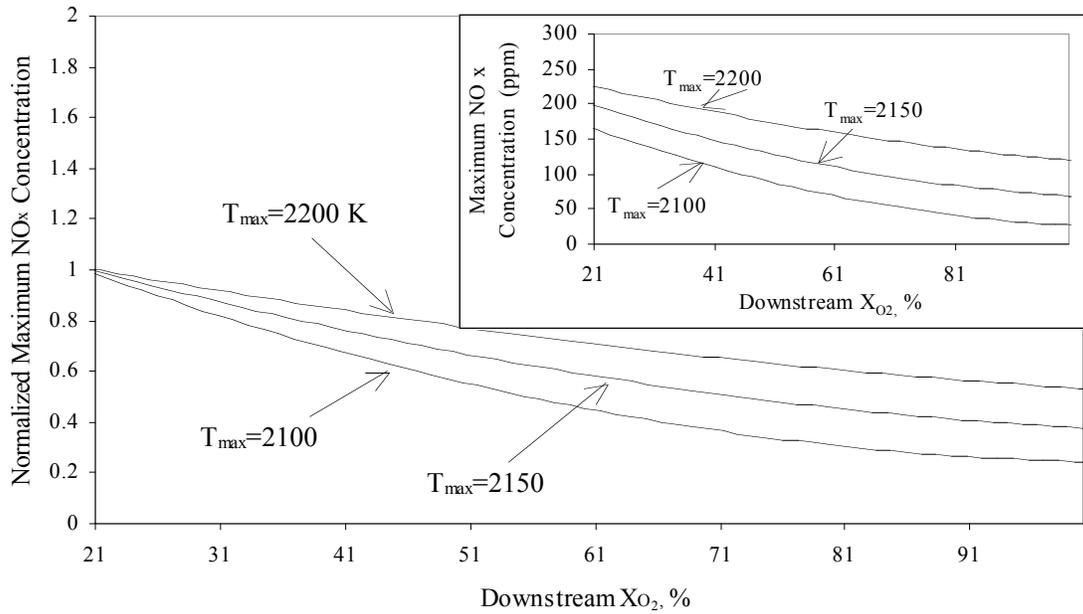


Fig. 20 Calculated maximum NO_x concentration as function of downstream X_{O₂} and T_{max} ($\phi > 1$, $u_{\text{exit}} = 150$ cm/s, $L = 1.4$ cm).

4.6 Efficiency Improvement in Gas Turbine Cycle

For the design calculations the technical concept studied is shown schematically in Fig. 21. The efficiencies calculations were carried out with STANJAN. The flue gas coming out from the turbine is utilized to preheat the air in the membrane module. There are a number of parameters to be potentially varied in this cycle. They include:

- The ratio R of the molar flow rate air passing through the membrane for oxygen enrichment to the total molar flow rate of air utilized.
- The membrane separation factor expressed as

$$S = \frac{(y_{O_2} / y_{N_2})_{\text{permeate}}}{(y_{O_2} / y_{N_2})_{\text{feed}}}$$

- The membrane productivity, expressed as

$$P = \frac{(F_{O_2})_{permeate}}{(F_{O_2})_{Feed}}$$

where (F_{O_2}) is the molar flow rate of oxygen.

- The equivalence ratio into the combustor defined as $\phi = \frac{(X_{CH_4} / X_{O_2})}{(X_{CH_4} / X_{O_2})_{Stoich}}$

where X_{CH_4} is the mole fraction of CH_4 in the feed in the combustor.

- The membrane operating temperature.

For the present calculations a real gas turbine (GE Frame 7F, operated by the Southern California Gas Company) was chosen. The total mass flow rate (under conditions of zero oxygen enrichment), the total CH_4 input, and pressure ratio values selected for the calculations represent the real operating conditions for this turbine. In all design simulations care must be taken that the temperatures reached anywhere in this turbine do not exceed the manufacturer's stated permissible temperatures. This temperature for the GE Frame 7F is listed to be ~ 1700 K. The equivalence ratio for all calculations reported here was taken to be 0.36. The turbine efficiency is defined as:

$$E(\%) = \frac{W_T - W_c}{Q_{total}},$$

where W_T is the turbine work done, W_C the compressor work needed, and Q_{total} the total heating value of CH_4 .

Figure 22 depicts the turbine efficiency as a function of R for various values of S for a fixed value of $P=0.9$. When the membrane separation factor increases, the efficiency of the gas turbine also increases. Also, when the ratio R increases, the turbine efficiency will also originally increase. However, beyond a certain value of R (>0.7), for membranes with high S the efficiency decreases. This is because for these cases one uses

up the waste heat available in the flue gas, and additional energy is, therefore, needed to heat up the membrane side air.

Figure 23 depicts the turbine efficiency as a function of R for various values of P for perfect membranes. When P increases the efficiency will also increase. For each P beyond a certain R the efficiency decreases. The reason for the drop of efficiency is the same as in Figure 22.

Figure 24 depicts 3-D plots of the turbine efficiency as a function of S and P for three different value of R of 0.1, 0.3, 0.5. When comparing the efficiency of the three cases, one concludes that the efficiency increases when R increases, as it was also shown in Figure 22 and 23. Higher S values will give higher efficiency, but the differences are not that great for $S > 10$.

Figure 25 depicts the effect of the temperature, at which the membrane module operates, for various values of R and fixed values of P (=0.9) and S (=1000). Obviously higher temperatures of operation result in reduced efficiencies, which points out the importance of developing membranes which will operate efficiently at low temperatures.

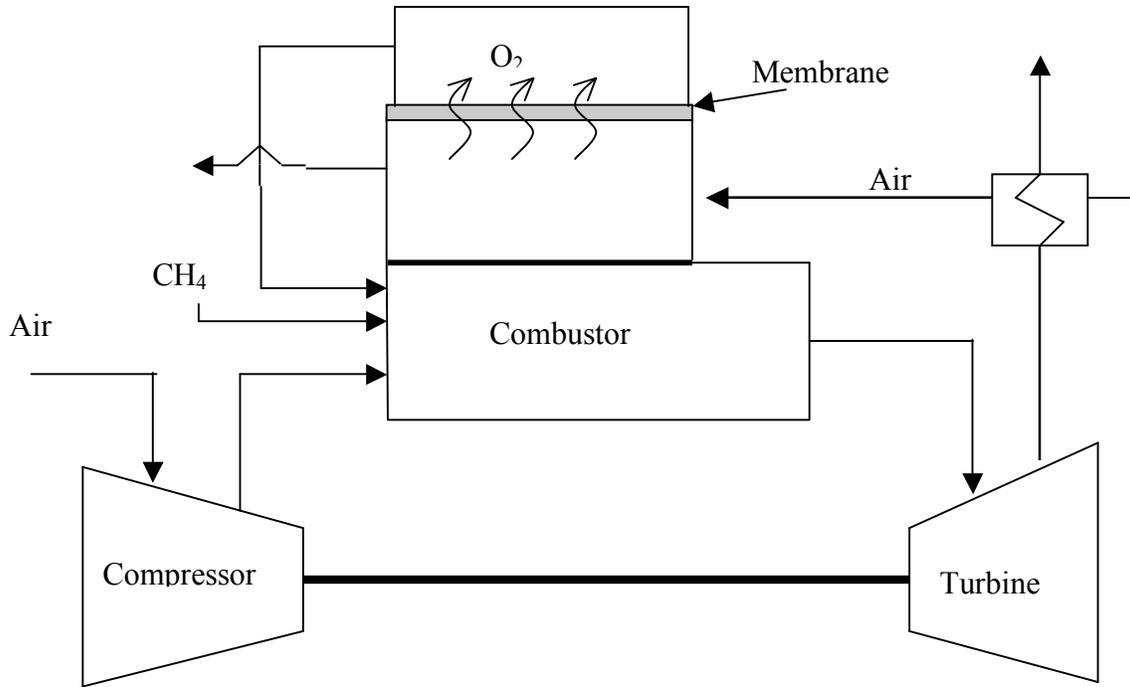


Fig. 21 Schematic of the OEC-based CRGT system

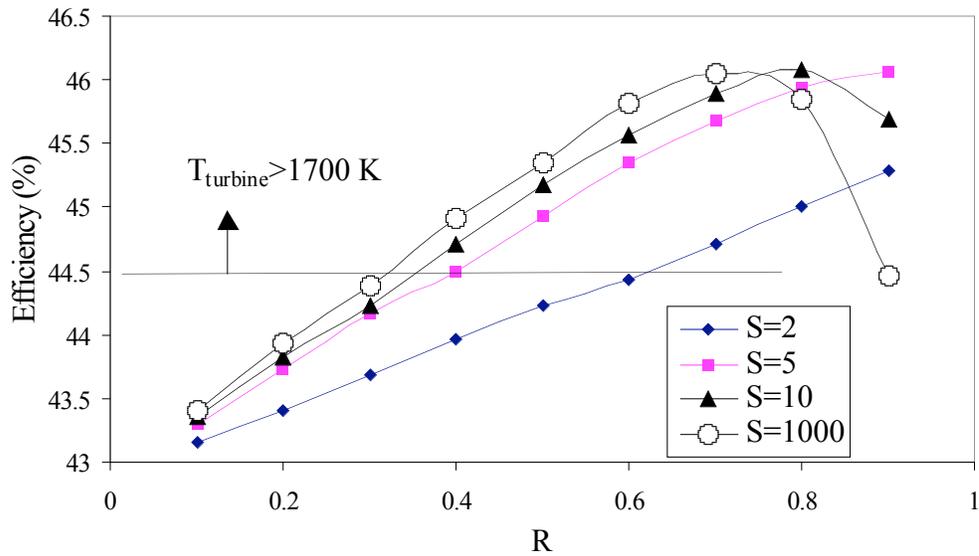


Fig. 22 Turbine efficiency as a function of R for various values of S for a fixed value of $P=0.9$ and a reactor temperature of 800 K ($T_{\text{turbine}} > 1700$ K for Efficiency $> 44.5\%$)

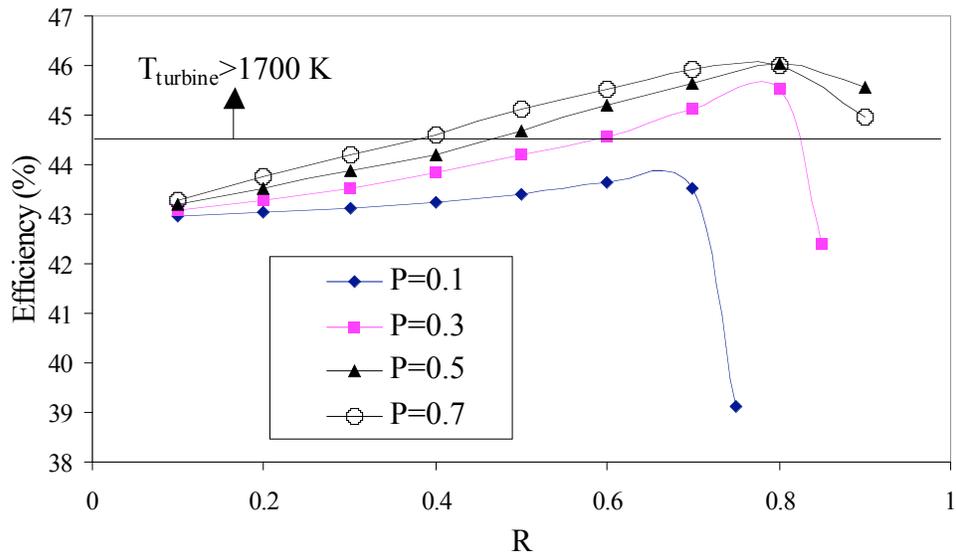


Fig. 23 Turbine efficiency as a function of R for various values of P for perfect membranes ($S \sim \infty$) and a reactor temperature of 800 K ($T_{\text{turbine}} > 1700 \text{ K}$ for Efficiency $> 44.5\%$)

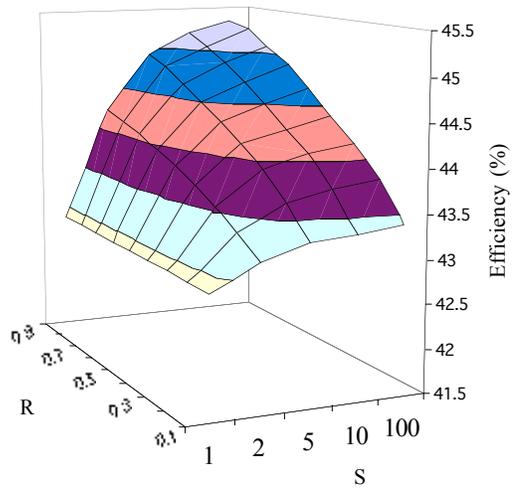


Fig 24a

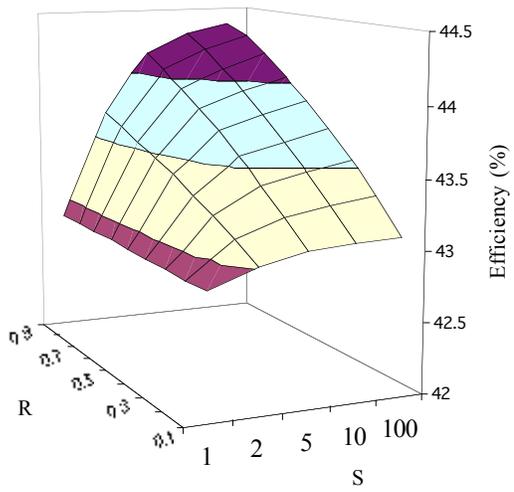


Fig 24b

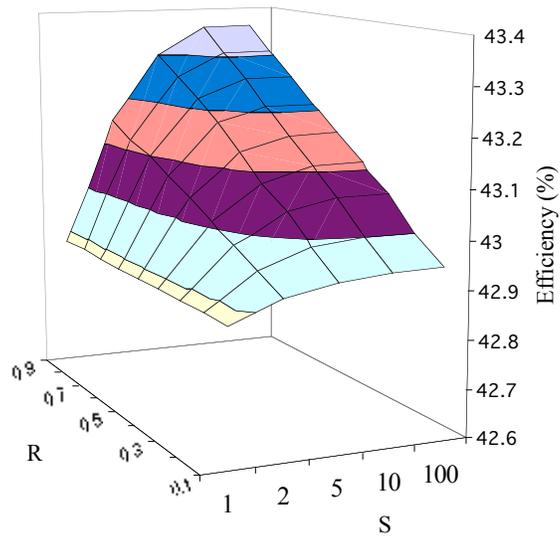


Fig 24c

Fig. 24 3-D plots of the turbine efficiency as a function of S and P for three different value of R of 0.1(Fig. 24a), 0.3(Fig. 24b), 0.5(Fig. 24c) and a reactor temperature of 800 K.

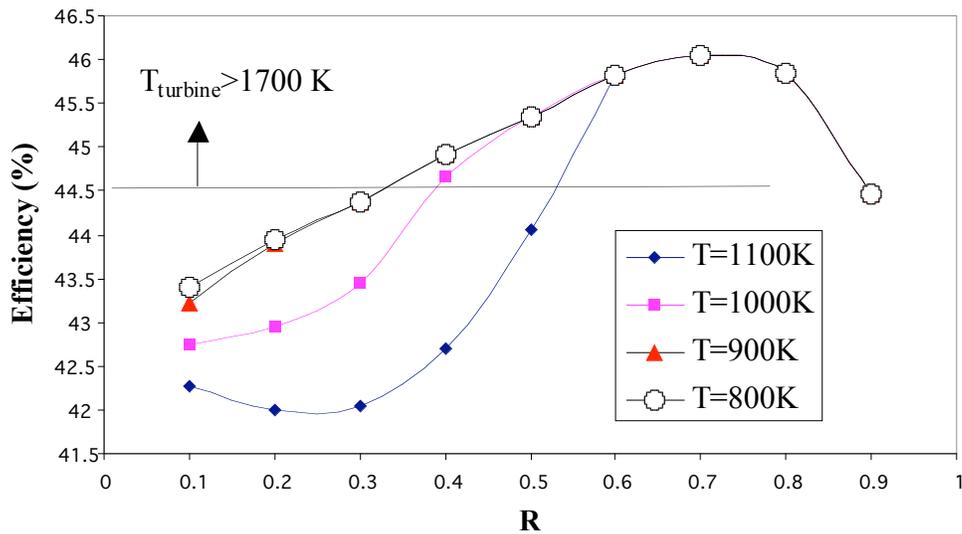


Fig 25 Turbine efficiency as a function of R for various values of membrane operation temperature for perfect membranes ($S=1000$) and $P=0.9$.

5 Conclusions

A combined experimental and detailed numerical investigation was conducted whose objective is to investigate the feasibility of a novel technical concept, which involves an combined OTM/OEC process in a membrane reactor with the aid of high-temperature solid-oxide membranes.

The key conclusions drawn from our investigation are as follows:

- Solid oxide dense oxygen conducting membranes, made of $\text{SrCo}_{0.5}\text{FeO}_3$ perovskite material, have been prepared and tested for their oxygen permeation characteristics. These membranes have been shown to be highly permeable to oxygen under conditions akin to the OEC combustion environment. The membranes prepared show satisfactory oxygen permeability and good stability during the permeation studies both in the presence of inert and reactive sweeps.
- Results on flame propagation revealed that O_2 enrichment can enhance combustion stability, since for the same flame temperature, the laminar flame speeds increase, and the flammability limits are extended.

- The analysis of the NO_x structures revealed that O₂ enrichment can be of value, as it results in reduced NO_x production for the same flame temperature. The reduction of NO_x production is caused by the synergistic effect of flame temperature reduction and N₂ concentration reduction, as more O₂ is added.
- We have reported on the preparation and characterization of the solid-oxide membranes, and on the fundamental combustion studies of the relevant reactive mixtures, including the effect of O₂ lancing on the NO_x and CO emissions of fuel-lean and fuel-rich CH₄/air premixed flames. The effect of downstream O₂ enrichment on the combustion characteristics of fuel-lean and fuel-rich CH₄/air flames was also investigated in the counterflow configuration.
- The efficiency of the hybrid OTM/OEC process has been studied. The efficiency improvement depends on the quality of membranes utilized. Membranes with poor separation characteristics or lower permeability show poor performance, as they require for their operation additional energy beyond what is available through the available waste heat. In fact use of inferior quality membranes is likely to result in a decrease in turbine efficiency.

6 Recommendations

The use of solid oxide membranes in power generation applications was proven technically feasible. In order to bring the technology to the commercial stage the following tasks should be conducted:

- Develop tubular solid oxide membranes so that the technology can be evaluated in a scaled-up membrane reactor.

- Test the long-term (>1 year) stability of tubular membrane.
- Carry out an extensive economic evaluation of the technology, including a detailed market survey.

7 Public Benefits to California

The concept feasibility of the proposed OTM/OEC process has been proven. With this know-how, the technology can be moved all the way from the “proof of concept” level to pilot plant scale demonstration, and to full-scale commercialization. Power generation is the primary focus of this project. Industrial furnaces and boilers, however, also represent another important potential application. What is learned here on the OTM/OEC technology will be of also of great value in these areas of application.

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**California Energy Commission
Energy Innovations Small Grant (EISG) Program
PROJECT DEVELOPMENT STATUS**

Questionnaire

Answer each question below and provide brief comments where appropriate to clarify status. If you are filling out this form in MS Word the comment block will expand to accommodate inserted text.

Questions	Comments:
Overall Status	
1) Do you consider that this research project proved the feasibility of your concept?	Yes.
2) Do you intend to continue this development effort towards commercialization?	Yes.
Engineering/Technical	
3) What are the key remaining technical or engineering obstacles that prevent product demonstration?	The key tasks are: <ul style="list-style-type: none"> To develop tubular solid oxide membranes so that the technology can be evaluated in a scaled-up membrane reactor. To test the long-term (>1 year) stability of tubular membrane. Carry out an extensive economic evaluation of the technology, including a detailed market survey.
4) Have you defined a development path from where you are to product demonstration?	Yes
5) How many years are required to complete product development and demonstration?	Depending on the availability of funding, 3-5 years.
6) How much money is required to complete engineering development and demonstration?	For a small- scale pilot-plant demonstration the estimated cost is \$300,000 - 500,000.
7) Do you have an engineering requirements specification for your potential product?	We have a rough idea of what the basic engineering requirements are. Further refinement has to come from the pilot-plant demonstration.
Marketing	
8) What market does your concept serve?	Primarily the high temperature furnace (glass, steel, incinerator, ...), boiler, and power plant industries.
9) Is there a proven market need?	We believe so, based on our discussions with various industry representatives. A more detailed market survey is, however, necessary before proceeding with further development.
10) Have you surveyed potential end users for interest in your product?	We have talked to a number of potential users. As part of any future development effort, we plan to carry out a more formal survey.

11) Have you performed a market analysis that takes external factors into consideration?	No, but again, as noted above, this will be one of the first tasks of any further developmental effort.
12) Have you compared your product with the competition in terms of cost, function, maintenance etc.?	Yes, we have compared the function and feasibility of our technology with competitive concepts for oxygen enhancement of air in the context of power/energy generation.
13) Have you identified any regulatory, institutional or legal barriers to product acceptance?	No, we do not foresee any regulatory or legal barriers. Based on our laboratory data our process would satisfy all the environmental regulations (NO _x , CO) in California.
14) What is the size of the potential market in California?	No data are available at this point. This is the information that potential future market surveys will generate.
15) Have you clearly identified the technology that can be patented?	In broad terms yes. As noted previously some key technical hurdles still remain.
16) Have you performed a patent search?	Yes.
17) Have you applied for patents?	No.
18) Have you secured any patents?	No.
19) Have you published any paper or publicly disclosed your concept in any way that would limit your ability to seek patent protection?	Yes on some of our preliminary data.
Commercialization Path	
20) Can your organization develop and produce your product without partnering with another organization?	As a University we will need industrial partners (membrane manufacturer, boiler/furnace/turbine manufacturers) to further develop and implement our product.
21) Has an industrial or commercial company expressed interest in helping you take your technology to the market?	We are talking to Media and Process Technology, Inc. of Pittsburgh PA about scaling up our membrane technology. We have recently jointly submitted a proposal for further technology development to the U.S. Department of Energy. We have discussed the process with the Gas Company of Southern California and with GTI.
22) Have you developed a commercialization plan?	No yet.
23) What are the commercialization risks?	Under evaluation.
Financial Plan	
24) If you plan to continue development of your concept, do you have a plan for the required	As previously noted, together with Media and Process Technology, Inc. we have submitted a proposal to the

funding?	U.S. Department of Energy. Further fundraising is planned over the next few months.
25) Have you identified funding requirements for each of the development and commercialization phases?	Yes for the membrane development and long-term testing. Only "rough" estimates for the field scale demonstration,
26) Have you received any follow-on funding or commitments to fund the follow-on work to this grant?	We are currently using internal USC funding for student support. As previously noted, we are currently seeking additional funding for the follow-on work.
27) Have you identified milestones or key go/no go decision points in your financial plan?	As a University we will need industrial backing for further development of this technology. Some of the key technical challenges have already been identified and represent key go/no go decision points for the overall project.
28) What are the financial risks?	See discussion above
29) Have you developed a comprehensive business plan that incorporates the information requested in this questionnaire?	No comprehensive business plan has been developed as yet. We have identified a key industrial partner and have also talked to other potential interested parties.
Public Benefits	
30) What sectors will receive the greatest benefits as a result of your concept?	Energy and power industries. The general public as a result of reduced environmental pollution from these industries.
31) Identify the relevant savings to California in terms of kWh, cost, reliability, safety, environment etc.	The laboratory data indicate increases in gas turbine efficiency in excess 1.5%, NO _x emissions decrease by 20-60% for fuel lean combustion ($\phi < 1$). NO _x emissions decrease by 40-70% and CO emissions decrease by 20-40% for fuel rich combustion ($\phi > 1$). For combustion processes, where pure oxygen is required, it has the potential of significant cost savings..
32) Does the proposed technology impact emissions from power generation?	Yes favorably, see discussion above
33) Are there any potential negative effects from the application of this technology with regard to public safety, environment etc.?	We do not believe so, based on the laboratory data. The long-term mechanical/thermal stability of the materials must be further validated, however.
Competitive Analysis	
34) Identify the primary strengths of your technology with regard to the marketplace.	Low emissions, increased efficiency, savings in the cost of oxygen production
35) Identify the primary weaknesses of your technology with regard to the marketplace.	Additional capital investment may be required for retrofitting existing facilities.
36) What characteristics (function, performance, cost etc.) distinguishes your product from that of your competitors?	Increased efficiency and combustion stability, and reduced pollutant emissions.
Development Assistance	
The EISG Program may in the future provide follow-on services to selected Awardees that would assist them in obtaining follow-on funding from the full range of funding sources (i.e. Partners, PIER, NSF, SBIR, DOE etc.). The types of services offered could include: (1) intellectual property assessment; (2) market assessment; (3) business plan development etc.	

<p>37) If selected, would you be interested in receiving development assistance?</p>	<p>As previously noted, we are currently pursuing follow-up funding with DOE. We would welcome any information the EISG program would provide on potential additional funding opportunities.</p>
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