

**APPLICATIONS OF OXY-FUEL COMBUSTION
TECHNOLOGY INTO GAS TURBINE COMBUSTORS
AND ION TRANSPORT MEMBRANE REACTORS**

BY

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To my Father, my Mother, my brother and my sisters

To my Sincere Wife and my Beloved daughters, Amira and Malak

To my future sons and daughters if any

To my professors Dr.Habib, Dr.Ben-mansour and Dr.El-Kassaby

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THESIS ABSTRACT

Name **Medhat Ahmed Abdallah Nemitallah**
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For decreasing greenhouse gas (mainly CO₂) emissions, several approaches have been evaluated and reviewed for capturing CO₂ in the utility industry, namely Carbon Capture and Storage technology (CCS). As a promising CCS technology, oxy-fuel combustion can be used in existing and new power plants. There are two main approaches available to utilize the oxy-combustion technology, one of them is the use of air separation units to separate O₂ which will be used in the combustion process and the other application is the ion transport membrane (ITM) reactor technology. The objective of this proposed work is to study in details the above mentioned two approaches for applications in oxy-fuel combustion technology. For the application of the first approach, experimental and numerical investigations on an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor are conducted. The combustor is fuelled with CH₄ and a mixture of CO₂ and O₂ as oxidizer. A wide range of operating parameters was considered aiming to determine the stability limits of the oxy-combustion diffusion flame and characterize the flame in detail. The experimental and numerical results showed that the stability of the oxy-combustion flame is affected when the operating percentage of

oxygen in the oxidizer mixture is reduced below 25 %. For the application of the second approach, from our understandings of the oxygen permeation and oxy-fuel combustion characteristics that come out from a 2D analysis of a simple symmetric ITM reactor, a new 3D reactor design is introduced for the substitution of ITM reactors into a gas turbine combustor. A new oxygen permeation equation model has been developed by fitting the experimental data available in the literature for a LSCF ion transport membrane. Based on the 3D analysis, the present proposed monolith structure design ITM reactor is capable of delivering power ranging from 5 to 8 MWe based on cycle first law efficiency.

**DOCTOR OF PHILOSOPHY DEGREE
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ملخص البحث

درجة الدكتوراة في الفلسفة

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الاسم:

تطبيقات تكنولوجيا الحرق بواسطة الأوكسجين في محركات التوربينات الغازية
ومحركات الأغشية الممررة للأيونات
الهندسة الميكانيكية

عنوان الرسالة:

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تاريخ التخرج:

لتقليل إنبعاثات الغازات المسببة للإحتباس الحرارى وخاصة غاز ثانى أكسيد الكربون، تم تقييم العديد من الوسائل لمنع خروج ثانى أكسيد الكربون للجو فى الصناعة وخاصة التكنولوجيا المسماة حيز ثانى أكسيد الكربون. تعتبر تكنولوجيا الحرق عن طريق الأوكسجين واحدة من التكنولوجيا الواعدة من تكنولوجيات أسر ثانى أكسيد الكربون والتي يمكن تطبيقها فى محطات الطاقة القديمة والحديثة. هناك طريقتان لإستخدام تكنولوجيا الحرق عن طريق الأوكسجين، إحداهما عن طريق إستخدام وحدة فصل الهواء لإنتاج الأوكسجين الذى يمكن إستخدامه للحريق داخل غرف الإحتراق والأخرى عن طريق تكنولوجيا محركات الأغشية الممررة للأيونات. الهدف من البحث الحالى هو إجراء دراسة تفصيلية على هاتين الطريقتين لتطبيق تكنولوجيا الحرق بواسطة الأوكسجين. لتطبيق الطريقة الأولى، تم إجراء التحليلات بإستخدام الطريقتين العملية والرقمية على لهب منتشر تحت الضغط الجوى داخل نموذج مصغر لمحرك توربينة غازية. غرفة الإشتعال تم إمدادها بوقود الميثان وخليط مؤكسد مكون من الأوكسجين وثانى أكسيد الكربون. تمت دراسة تأثيرات عدد كبير من العوامل فى هذا البحث أملا فى دراسة إستقرار لهب الحرق بالأوكسجين وتحليل اللهب بالتفصيل. أظهرت نتائج الدراساتين العملية والرقمية أن إستقرار لهب الحرق بالأوكسجين يتأثر كثيراً عندما تقل نسبة الأوكسجين فى الخليط المؤكسد عن 25 فى المائة. لتطبيق الطريقة الثانية، من خلال فهمنا لعملية مرور الأوكسجين خلال الغشاء وكذلك عملية الحرق بواسطة الأوكسجين عن طريق إجراء تحليلات ثنائية الأبعاد لمحرك غشاء ممرر للأوكسجين بسيط ومتماثل، تم عمل تصميم ثلاثى الأبعاد لمحرك غشاء ممرر للأوكسجين لإستخدامه بدلا من غرفة الإحتراق العادية فى محركات التوربينات الغازية. تم تطوير معادلة لمرور الأوكسجين

خلال الغشاء باستخدام البيانات المتاحة فى الأبحاث المنشورة سابقاً لمحرك غشاء LSCF الممرر للأيونات. من خلال الدراسة ثلاثية الأبعاد، فإن التصميم الحالى للمحرك الغشائى قادر على إنتاج قدرة من 5 إلى 8 ميغاوات بناءً على الكفاءة المحسوبة من خلال القانون الأول للديناميكا الحرارية.

درجة الدكتوراة فى الفلسفة
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CHAPTER 1

INTRODUCTION

Global climate change is one of the greatest challenges in the 21st century. The greenhouse gas making the largest contribution to global climate change from human activities is carbon dioxide (CO₂). CO₂ emissions from the fossil fuel-based large power plants are of main concern as they are the largest sources of CO₂ in the coming decades. International Energy Agency forecasts have indicated that some 38 percentage of the world's electricity will still be generated from coal by 2020 [1]. For decreasing greenhouse gas (mainly CO₂) emissions, several approaches have been evaluated and reviewed for capturing CO₂ in the utility industry, namely Carbon Capture and Storage technology (CCS), including pre-combustion capture, oxyfuel combustion, and post-combustion capture. As a promising CCS technology, oxyfuel combustion can be used in existing and new power plants [2]. Compared to conventional air combustion, oxyfuel combustion shows different characteristics of heat transfer, ignition, char burnout as well as NO_x emission [3]. During oxyfuel combustion, a combination of oxygen and recycled flue gases are used for combustion of the fuel. The exhaust gases consisting mainly of CO₂ and H₂O generated with a concentration of CO₂ ready for sequestration. The recycled flue gases used to control flame temperature and make up the volume of the

missing N_2 to ensure there is enough gas to carry the heat through the boiler. CO_2 capture and storage by the current technically viable options (post-combustion capture, pre-combustion capture and oxyfuel combustion) will impose a 7–10% efficiency penalty on the power generation process. The major contributors to this efficiency penalty are oxygen production and CO_2 compression. Cryogenic air separation systems use intricately designed multi-stage distillation processes at low temperature and require a significant amount of electrical power, mainly for air compression [4]. Typical electrical power requirements range from 160 kWh [5], to 270 kWh per ton of O_2 [6] with a commonly cited approximate value of 200 kWh per ton, depending on the desired purity. Despite their complexity, commercial cryogenic units achieve low Second Law efficiencies in the range of 15-24% [7], resulting in a First Law efficiency loss of up to 8.5% points compared to a typical NGCC (Natural gas combined cycle) without CCS [8]. Clearly, the thermodynamic and economic penalties incurred by the use of a cryogenic air separation process could easily offset any advantages gained by using Oxy-fuel CCS, prompting many researchers to investigate the use of alternative air separation systems.

Today, most of the researchers in the oxy-combustion field are working on combustion using mixed ionic and electronic conducting ceramic membranes. These membranes have received increasing interest from academia and industry. A major industrial effort is currently devoted to the development of the mixed-conducting ceramic membrane reactor technology for partial oxidation of hydrocarbons, in particular, partial oxidation of methane to syngas [9,10]. The membrane materials studied most extensively are lanthanum cobaltite perovskite type ceramics [10,11]. New mixed-conducting ceramic

membrane materials developed recently for the membrane reactor applications include modified perovskite ceramics having general formula of $\text{SrFeCo}_{0.5}\text{O}_x$ [12], brownmillerite structured ceramic represented by $\text{Sr}_{1.4}\text{La}_{0.6}\text{GaFeO}_{3-\delta}$ [13], and ceramic–metal dual phase membranes, such as $\text{Sr}_{0.2}\text{La}_{0.8}\text{Fe}_{0.69}\text{Co}_{0.1}\text{Cr}_{0.2}\text{Mg}_{0.01}\text{O}_3 + 50\text{Ag}/50\text{Pd}$ [14], and thin dual phase membranes consisting of the chemically stable yttria-stabilized zirconia (YSZ) and Pd phases [15]. All these membranes are oxygen semi-permeable with high oxygen permeation flux when the membrane is exposed to air and a hydrocarbon such as methane.

In order to decrease CO_2 emissions, many approaches have been evaluated in order to capture CO_2 , namely Carbon Capture and Storage technology (CCS). As a promising CCS technology, oxy-fuel combustion can be used in existing and new power plants. In oxy-combustion, a fuel is oxidized in a nearly nitrogen-free, diluted mixture such that the products consist mainly of CO_2 and water vapor, enabling a relatively simple and inexpensive condensation separation process facilitating CO_2 capture. There are two main approaches available to utilize the oxy-combustion technology, one of them is through the use of air separation units to separate O_2 which will be used in the combustion process and the other application is the ion transport membrane (ITM) reactor technology. The objective of this research work is to study in detail the above mentioned two approaches for applications of oxy-fuel combustion technology.

1.1 Background

The combustion of fuel in a mixture of recirculated flue gas (RFG) and oxygen, however, presents new challenges to combustion specialists. Several experimental investigations with oxy-firing pulverized coal burners reported that flame temperature and stability are strongly affected [3,16]. The substitution of N_2 with CO_2 in the oxidizer will lead to a reduction of the flame speed as reported by Zhu et al. [17]. This causes poor combustion performance and a modified distribution of temperature and species in the combustion chamber. Liu et al. [18] have performed numerical investigations on the chemical effects of CO_2 . A comparison between numerical and experimental data showed that the decrease in burning velocity for the oxyfuel combustion cannot entirely be described by only considering the material properties of CO_2 . Anderson et al. [19] have performed experiments on a 100 kW test unit which facilitates O_2/CO_2 combustion with real flue gases recycle. The tests comprise a reference test with air and two O_2/CO_2 test cases with different recycled feed gas mixture concentrations of O_2 (OF 21 @ 21 vol.% O_2 , 79 vol.% CO_2 and OF 27 @ 27 vol.% O_2 , 73 vol.% CO_2). The results showed that the fuel burnout is delayed for the OF 21 case compared to air-fired conditions as a consequence of reduced temperature levels. Instead, the OF 27 case results in more similar combustion behavior as compared to the reference conditions in terms of in-flame temperature and gas concentration levels, but with significantly increased flame radiation intensity.

On the other hand, Teraoka et al. [20] first demonstrated that $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ oxide-based perovskite-type ceramic membranes have appreciably high oxygen permeation fluxes at high temperatures. Following Teraoka et al.'s work, many researchers studied the La–Sr–Co–Fe series as oxygen permeable membranes [21-28]. The oxygen ionic

transference number obtained was in the range of 10^{-5} to 10^{-3} depending on the temperature and ambient atmosphere, and the activation energy for ionic transport was 64–125 kJ/mol. Inconsistencies (up to one order of magnitude) were frequently reported on the oxygen permeation rates even with nominally identical membrane materials. For example, Teraoka et al. [20] reported the oxygen permeation flux as high as 2.31×10^{-6} mol/cm²s at 850°C for the SrCo_{0.8}Fe_{0.2}O_{3-δ} membrane; while the oxygen permeation fluxes for SrCo_{0.8}Fe_{0.2}O_{3-δ} membrane of the same thickness from Kruidhof et al. [21] and Qiu et al. [22] are 1.8×10^{-7} and 6.3×10^{-7} mol/cm²s, respectively, under the same experimental conditions. In membrane reactor applications in which the membrane is, respectively, exposed to air and methane, the difference in the oxygen permeation fluxes reported by different research groups could be as large as two orders of magnitudes even for membranes of same or similar compositions [9,10,23-27].

To satisfy our objective regarding the application of oxy-combustion technology in conventional combustors, experimental and numerical investigations of an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor are presented. Oxy-combustion and emission characterization, flame stabilization and oxy-combustion model validation analyses are the main goals of the present work. The combustor is fuelled with CH₄ and a mixture of CO₂ and O₂ as oxidizer. Wide ranges of different operating parameters are considered including equivalence ratio, percentage of O₂/CO₂ in the oxidizer mixture, and fuel volume flow rate. The study aims to check the stability of the oxy-combustion diffusion flame experimentally and numerically and also to check the minimum permissible percent of O₂ in the oxidizer mixture required in order to get a stable flame. Visualizations of the flame at the above mentioned operating conditions

have been carried out experimentally and comparisons with the numerical results have been done. The flames have been characterized in details by measuring the exhaust gas temperatures and comparing them with those from the numerical model. Flame zone also has been characterized in details by plotting the axial and radial temperatures, species concentrations and flow velocities. A modified two-step oxy-combustion reaction kinetics model for methane-oxygen combustion has been used in order to predict a clearer oxy-combustion characteristics and then more accurate numerical results in order to correctly validate the numerical model using the experimental results.

Computational fluid dynamics (CFD) is becoming an important industrial tool for trouble-shooting and optimization. However, CFD modeling of industrial combustion applications is a computationally demanding task [29]. Because of this, almost it is necessary to apply simplified reaction mechanisms to reduce the computing cost and time; however the simplified schemes cannot be expected to work as well under oxy-fuel combustion conditions like the case of combustion using air. For conducting the 2D analysis of the simple symmetric design ITM reactor, the modified two step finite rate oxy-combustion reaction kinetics model done by Andersen et.al. [29] is used to predict a oxy-combustion characteristics inside a stagnation flow ITM reactor. A detailed study is presented here to understand the performance of ion transport membranes under the oxy-combustion conditions in the permeate side of the membrane. Effects of many parameters including inlet gases temperature, reactor geometry, feed and sweep flow rate, oxygen partial pressure in the feed side and the effect of the percentage of CH_4 in the sweep gases mixture on the permeation and combustion processes are included in this work.

From our understanding of the oxygen permeation and oxy-fuel combustion characteristics that come out from a 2D analysis of a simple symmetric ITM reactor, a new 3D reactor design is introduced for the substitution of ITM reactors into a gas turbine combustor. Little work was reported with a focus on examining the effects of reaction side conditions and flow configuration on oxygen permeation through the mixed-conducting ceramic membranes and none has been performed for 3-D membrane reactors. In the present study, focus is made on oxygen separation through ion transport membranes and then the combustion is made in the permeate channels with fuel in a mixture of $O_2/CO_2/H_2O$. The new reactor design introduced here is substituting conventional gas turbine combustor by a monolith structure ITM reactor. Optimization for the feed and sweep flow rates have been done in order to meet the power required for the reactor and keeping the reactor size as compact as possible. Effects of flow configurations, channel width and percentage of CH_4 in the permeate side flow are also introduced under constant inlet gas temperature and fixed operating pressure of 10 bars. The reactor geometry has been optimized based on the optimization of channel width. Accordingly, the number of permeate and feed channels has been calculated keeping the reactor size as close as possible to the size of a real industrial gas turbine. The monolith structure reactor design introduced here is able to give power ranging from 5 to 8 MWe based on cycle first law efficiency.

1.2 Objectives of the present research work

Based on the above details, the objectives of the present research work are considered as follows:

- ✓ Investigate experimentally and numerically the atmospheric diffusion oxy-combustion in a gas turbine model combustor.
- ✓ Determine flame stability under wide operating range of parameters including equivalence ratio, percentage of O_2/CO_2 in the oxidizer mixture in addition to fuel volume flow rate.
- ✓ Define the minimum percentages of O_2 in the oxidizer mixture required to get a stable oxy-flame.
- ✓ Characterize experimentally the flames in detail by obtaining the main species concentration at the exhaust section of the combustor, exhaust temperature and inside reactor temperature distribution which can serve as a database for combustion models validation.
- ✓ Validate the numerical model using the experimental data.
- ✓ Investigate in detail the oxygen permeation process and oxy-fuel combustion characteristics inside an ITM reactor using a simple symmetric design reactor allowing the reduction of the number of coordinates to 2D without reducing the accuracy of the solution.
- ✓ Conduct a detailed sensitivity analysis for all of the parameters affecting the membrane reactor performance.

- ✓ Develop new oxygen permeation equation model and perform the reaction kinetics using a two-step oxy-combustion reaction kinetics model.
- ✓ Develop based on the results obtained from the 2-D analysis, a new 3-D reactor design for the substitution of gas turbine combustor by an ITM reactor utilizing an ITM monolith structure reactor.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon capture technologies

Energy production from fossil fuel combustion results in the emission of greenhouse gases, the dominant contributor being CO₂. Public awareness and legislation have led to a policy of reduction of greenhouse gas emissions in most economically well-developed countries, with the regulations partially driven by (international) initiatives such as the Kyoto protocol and the Inter-governmental Panel on Climate Change [30]. Greenhouse gas emissions from energy production can be reduced by the use of alternative energy sources such as nuclear power and renewable energy. Renewable energy sources are increasingly used, however, until these sources can reliably produce significant amounts of energy, the immediate energy demand is likely to be met by conventional fossil fuel combustion, as indicated by energy policies and use projections. To reduce greenhouse gas emissions from fossil fuel-fired power generation, several possibilities exist [3]: (1) Improving efficiency of power plants, (2) Introduction of combined cycles with generation by gas and steam turbines, which can achieve high thermal efficiencies, (3) replacement of fossil fuels with renewable resources, (4) Substitution of coal by natural gas (having a lower carbon content), and finally (5) CO₂ capture and storage (called

CCS). Incremental reduction of greenhouse gas emissions can be achieved by the first four options, however, to make a step-change reduction in emissions, the CO₂ generated from combustion needs to be captured and stored (or sequestered).

All technologies include compression of the CO₂ product to a supercritical state, typically 10 MPa, prior to transport and geological storage at a depth (and thereby pressure) retaining this state. Three main methods can be envisaged for the capture of CO₂ with these three systems as shown in Fig.2.1:(1) pre-combustion capture: to capture CO₂ in a synthesis gas after conversion of CO into CO₂; (2) post-combustion capture: to capture CO₂ in the exhaust gases once the fuel has been fully burned with air; (3) capture in oxy-combustion: consisting of combustion in oxygen with recycling of exhaust gases (therefore, composed mainly of CO₂ and water) and purification of the CO₂ flow, to eliminate incondensable gases.

The literature shows (see Fig.2.2) that the highest efficiency with capture is obtained for NGCC with post-combustion capture, with an efficiency of 50% compared with 60% without capture. The next highest is the oxy-combustion in PC, with an efficiency of almost 35% compared with 45% without capture, and then IGCC-Puertollano with pre-combustion capture with an efficiency of the order of 33.5% compared with 44% without capture. The lowest efficiency is obtained with post-combustion capture in PC, equal to 30% which is 15 points less than PC without capture (if MEA is used) [31]. Therefore, from a purely energetic point of view without considering economic figures, it would be

recommended to only consider pre-combustion capture in IGCC, post-combustion in NGCC and oxy-combustion in PC.

2.2 Oxy-fuel combustion characteristics

The characteristics of oxy-fuel combustion with recycled flue gas differ with air combustion in several aspects primarily related to the higher CO₂ levels and system effects due to the recirculated flow, including the following [3]: (1) To attain a similar adiabatic flame temperature (AFT), the O₂ proportion of the gases passing through the burner is higher, typically 30%, than that for air (of 21%), necessitating that about 60% of the flue gas is recycled. (2) The high proportions of CO₂ and H₂O in the furnace gases result in higher gas emissivities, so that similar radiative heat transfer for a boiler retrofitted to oxy-fuel will be attained when the O₂ proportion of the gases passing through the burner is less than the 30% required for the same AFT. (3) The volume of gases flowing through the furnace is reduced somewhat, and the volume of flue gas (after recycling) is reduced by about 80%. (4) The density of the flue gas is increased, as the molecular weight of CO₂ is 44, compared to 28 for N₂. (5) Typically, when air-firing coal, 20% excess air is used. Oxy-fuel requires a percent excess O₂ (defined as the O₂ supplied in excess of that required for stoichiometric combustion of the coal supply) to achieve a similar O₂ fraction in the flue gas as air firing, in the range of 3– 5% [32]. (6) Without removal in the recycle stream, species (including corrosive sulphur gases) have higher concentrations than in air firing. (7) As oxy-fuel combustion combined with sequestration must provide power to several significant unit operations, such as flue gas compression, that are not required in a conventional plant without sequestration, oxy-fuel combustion/ sequestration is less efficient per unit of energy produced.

2.2.1 Reaction and emissions characteristics

The combustion of fuel in a mixture of recirculated flue gas (RFG) and oxygen, however, presents new challenges to combustion specialists. Several experimental investigations with oxy-firing pulverized coal burners report that flame temperature and stability are strongly affected [33,34]. This work focuses on the investigation of the oxy-combustion of methane to see the effect of CO₂ recirculation on combustion characteristics. The substitution of N₂ with CO₂ in the oxidizer will lead to a reduction of the flame speed as reported by Zhu et al. [35]. This causes poor combustion performance and a modified distribution of temperature and species in the combustion chamber.

Liu et al. [18] have performed numerical investigations on the chemical effects of CO₂. A comparison between numerical and experimental data showed that the decrease in burning velocity for the oxyfuel combustion cannot entirely be described by only considering the material properties of CO₂. CO₂ affects the combustion reactions especially by the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$. The competition of CO₂ for H radical through the above reverse reaction with the single most important chain branching reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ significantly reduces the concentrations of important radicals, i.e. O, H, and OH, leading to significant reduction of fuel burning rate. This hypothesis is supported by a comparison of the burning velocity of methane flames and hydrogen flames in a CO₂/O₂ gas mixture.

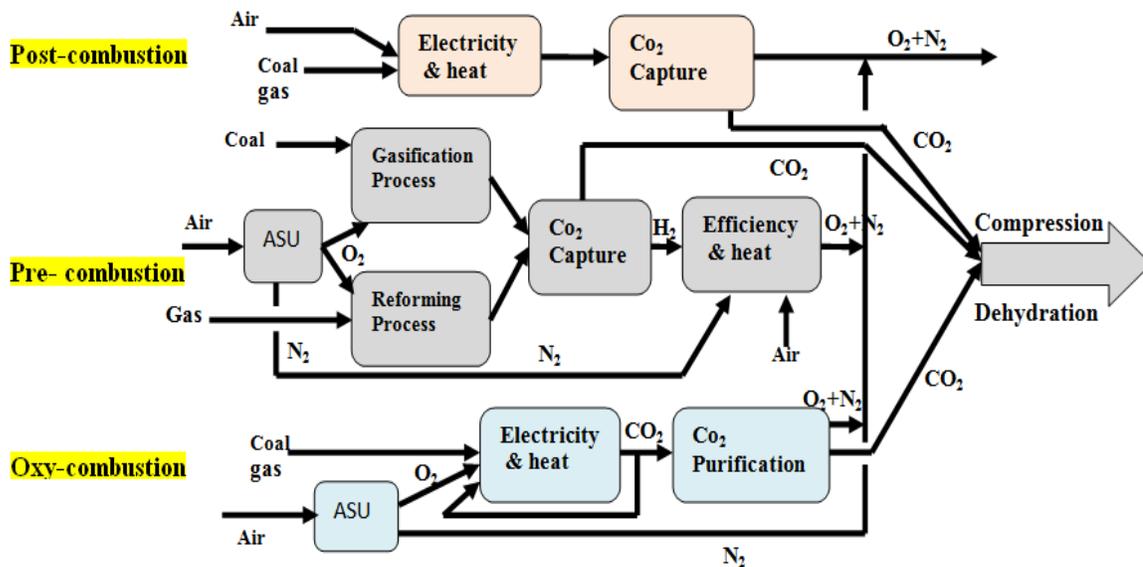


Figure 2.1 The three capture processes of CO₂ [31].

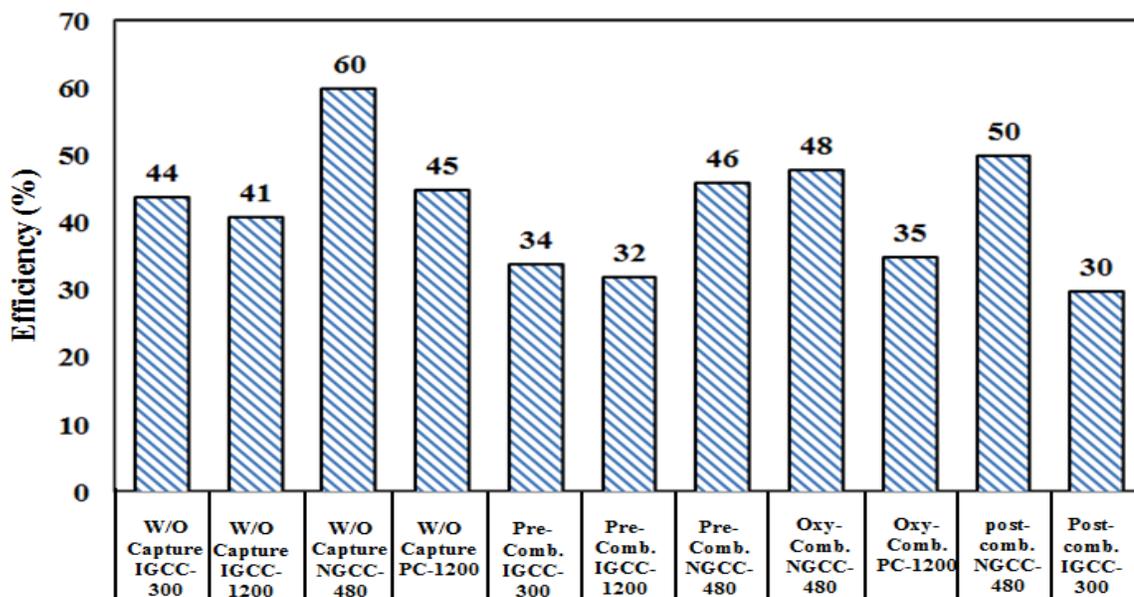


Figure 2.2 Efficiency of the different systems with and without CO₂ capture [31].

The influence of CO₂ on the burning velocity of hydrogen flames is less significant because the concentration of hydrogen radicals is much higher. Finally, it was summarized, that the chemical effect of CO₂ significantly reduces the burning velocity of methane, where by the relative importance of this chemical effect increases with increasing CO₂ concentration in the oxidizing mixture. Anderson et al. [19] have performed experiments in a 100 kW test unit which facilitates O₂/CO₂ combustion with real flue gas recycle. The tests comprise a reference test in air and two O₂/CO₂ test cases with different recycled feed gas mixture concentrations of O₂ (OF 21 @ 21 % O₂, 79 % CO₂ and OF 27 @ 27 % O₂, 73 vol.% CO₂). The results show that the fuel burnout is delayed for the OF 21 case compared to air-fired conditions as a consequence of reduced temperature levels. Instead, the OF 27 case results in more similar combustion behaviour compared to the reference conditions in terms of in-flame temperature and gas concentration levels, but with significantly increased flame radiation intensity.

During oxy-fuel combustion, the amount of NO_x exhausted from the system can be reduced to less than one-third of that with combustion in air [16,36,37]. The NO_x reduction is thought to be the result of several mechanisms [38]: Decrease of thermal NO_x due to the very low concentration of N₂ from air in the combustor, the reduction of recycled NO_x as it is reburnt in the volatile matter release region of the flame, and the reaction between recycled NO_x and char. Okazaki and Ando used a bench-scale reactor to examine the effects of the latter two factors during oxy-fuel combustion with an O₂ concentration of 21% (i.e., recycling ratio as high as 80%) at a maximum flame temperature of 1450 K [38]. They concluded that the reduction of recycled NO_x is the

dominant mechanism for the reduction in NO_x emissions. They estimated that more than 50% of the recycled NO_x was reduced when 80% of the flue is recycled. It has also been found that oxy-fuel combustion can decrease the SO_2 emissions compared to that in air combustion [36,39].

2.2.2 Oxy-combustion systems

The concept of oxy-combustion involves the burning of fuel in pure oxygen in addition to some recycled flow gases or steam in order to control the flame temperature. The aim is to obtain a carbon dioxide-rich stream that is ready for sequestration, after removing water vapor and other impurities. Various oxy-combustion systems have been introduced in the literature [40,41-44]. The first version is the atmospheric pressure oxy-combustion system where part of the flue gases is recycled in order to control the flame temperatures. There is another alternative to using recycled flue gases is to inject steam in order to control the flame temperature [42]. To further increase the performance of these systems, pressurized systems have been proposed for both systems oxy-combustion with recycled flue gases [43,45-49] and oxy-syngas combustion in combination with solid fuel gasification technology [44]. There is also a recent technology which is the ion transport membrane reactor technology that can also be applied and it is discussed in details later on. The atmospheric oxy-coal combustion system shown in Fig.2.3 was introduced as a short-term solution to retrofit existing coal-fired power plant to include the option of carbon capture and sequestration. The additional required equipments as compared with air-fired systems are considered as discussed in the following sections.

2.2.2.1 Air Separation Unit

When retrofitting existing power plants to be used with oxy-combustion, the system uses the same equipments used in the conventional combustion in addition to an ASU used to produce an oxygen rich stream for combustion. Currently, the only ASU technology that can meet the volume and purity demand of a large scale coal-fired utility boiler is based on cryogenic distillation. Air is compressed, cooled and cleaned prior to being introduced into the distillation column to separate air into an oxygen-rich stream and a nitrogen-rich stream [51]. Cryogenic air separation is consuming about 0.24 kWh/kg O₂ with 95% oxygen purity [52,53]. The oxygen purity requirement for oxy-coal combustion (85-98%) is lower than that needed in the process industry (99.5-99.6%) [54]. The ASU can consume more than 15% of the gross power output [52,55-57].

2.2.2.2 Carbon dioxide purification unit

A carbon purification unit consists of gas cleanup units in order to remove water and other gases from the flue gas before being compressed for the sequestration process. Because oxy-combustion is compatible with retrofits, selective catalytic reduction (SCR), electrostatic precipitator (ESP) and flue gas desulphurization (FGD) are typically retained as means of NO_x, particulate matter and SO_x removal from the flue gases. These pollutants control devices are also suitable for use in conjunction with amine-type absorbents for post-combustion capture plants [51].

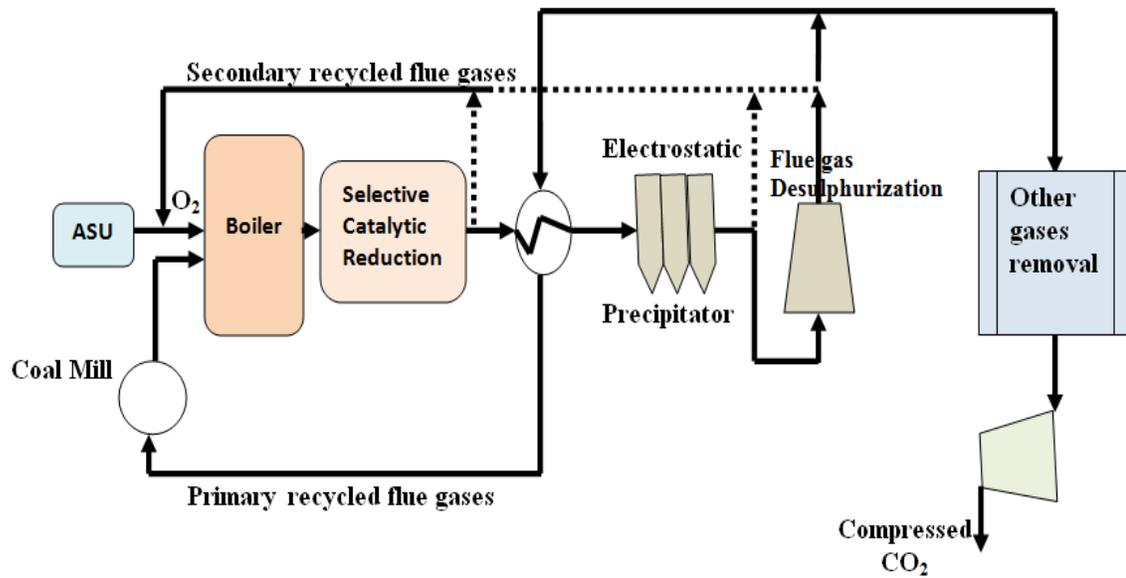


Figure 2.3 Atmospheric oxy-coal combustion system with flue gas recycle proposed for carbon capture in coal power plants based on the work in [40,50].

After the removal of acid gases such as SO_x and NO_x, non-condensable N₂, O₂, and Ar should also be purged using a non-condensable gas purification unit. This unit is made of multi-stage compression units with inter-stage cooling in order to separate out the inert gases.

2.2.2.3 Flue gas recirculation system

Recycled flue gases are required for replacement of nitrogen in order to control the combustion temperature. These flue gases can be recycled at different locations downstream of the economizer in the form of wet or dry recycles. since SO₂ concentration in the flue gas may accumulate due to flue gas recycle, resulting in two or three times higher concentration than in conventional air-firing systems, the primary recycle has to be at least partially desulphurized for medium and high sulfur coal, to avoid corrosion in the coal mill and flue gas pipes.

2.3 Oxy-combustion alternatives

Capture of CO₂ from large point sources such as power plants with subsequent geological storage offers the possibility of a significant and relatively quick response to climate change at a reasonable cost. Successful commercialization of such technology could therefore provide a transition to a future during which energy production from non-fossil energy sources can grow over time. At present, there are no power plants with CO₂ capture available on a commercial scale, but long time aquifer storage is currently applied

and evaluated in the North Sea and show promising results [58]. The CO₂ could also be stored in connection to enhanced oil recovery (EOR). Such storage has been closely monitored in the Weyburn project in Canada, see e.g. [59]. The highest cost is however on the capture side and to reduce the specific costs for capture different concepts are discussed. To recover and store carbon dioxide from flue gases of fossil fuel power plants, processes based on oxy-combustion appear to be promising. Concept of the technology is the combustion with commercially pure oxygen to achieve high CO₂ concentrations in the flue gases for the final CO₂ separation. The required oxygen is supplied by an air separation unit where the nitrogen is separated from the air. A great portion of the flue gases has to be recycled to substitute the removed nitrogen. This measure is inevitable to maintain the temperature level in the combustion chamber and in particular not to increase the heat transferred to the membrane walls of the steam generator which is limited by material parameters [60].

In the past decades, intense research efforts have been directed to the development and improvement of ceramic-based membranes for oxygen separation from air at high-temperature operations. Ceramic based membranes for oxygen separation systems can be categorized into pure oxygen conducting membranes and mixed ionic–electronic conducting membranes. Mixed ionic and electronic conducting ceramic membranes have received increasing interest from academia and industry. A major industrial effort is currently devoted to the development of the mixed-conducting ceramic membrane reactor technology for partial oxidation of hydrocarbons, in particular, partial oxidation of methane to syngas [9,10].

2.3.1 Utilization of air separation unit and conventional combustion chamber

The required oxygen in this case is supplied by an air separation unit where the nitrogen is separated from the air. A great portion of the flue gases has to be recycled to substitute the removed nitrogen. Key component of the oxy-fuel process with high temperature membrane air separation unit (HTM-ASU), which is in the stage of development, is a dense membrane made of ceramic materials. These materials begin to conduct oxygen ions above a material dependent temperature (usually above 700 °C). Driving force for the mass transport is the differential oxygen partial pressure across the membrane, while the oxygen flux is enhanced with decreasing membrane thickness and rising temperature. As only oxygen permeates the membrane, 100 % pure oxygen could be produced provided that air leakage within the membrane module is avoided. For further details regarding membrane materials, references [61,62] are recommended. The basic idea of the HTM-ASU, as illustrated schematically in Fig.2.4, is the elevation of the oxygen partial pressure on the air side with an air compressor. The partial pressure difference across the membrane can be further enhanced by lowering the oxygen partial pressure on the oxygen receiving side of the membrane by sweeping with flue gas, which contains only a small amount of oxygen. As temperatures at the compressor outlet are not sufficient to activate the membrane material's conduction mechanism, the air needs to be preheated with counter current oxygen enriched flue gas. To recover parts of the spent energy for compression, the oxygen depleted air is expanded in a turbine. As the off-gas leaves the HTM-ASU at still elevated temperatures, the heat can be recovered in the power plant cycle. The energy demand of the HTM-ASU is determined by the required

high temperature heat. In addition, mechanical driving power is needed or produced depending on the ASU process parameter design.

2.3.1.1 Applications of Oxy-fuel combustion in gas turbines

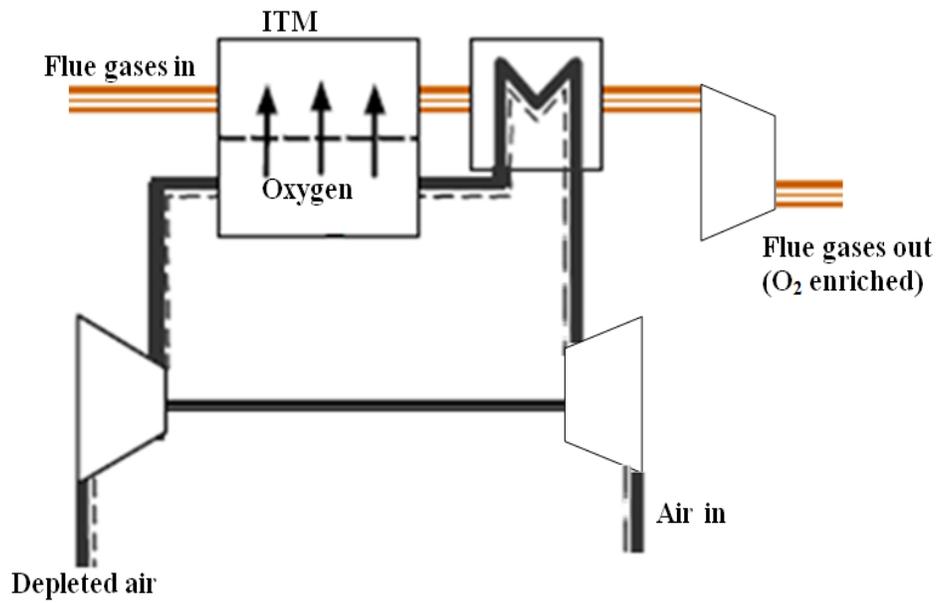
General characteristics. As an option to get O_2 required for combustion, Oxygen may be obtained via air separation units, e.g. cryogenic or membrane based processes. The combustion process takes place in nitrogen free or low-nitrogen environment resulting in a flue gas composed mainly of CO_2 and H_2O , as well as a low concentration of impurities such as argon and oxygen. Therefore, a simplified flue gas processing by means of condensation of H_2O to capture CO_2 , without using costly separation methods such as chemical absorption, can be possible. There are several proposed combined cycle concepts in oxy-fuel gas turbine processes with natural gas combustion in oxygen and CO_2 , for example, the O_2/CO_2 cycle [63-65], the COOLENERG cycle [66], the COOPERATE cycle [67], and the MATIANT cycle [68]. These cycles belong to the group also known as Semi-Closed Oxy-Fuel Combustion Combined Cycles (SCOF-CC). Recent studies within the European Union funded research project ENCAP (Enhanced Capture of CO_2) have concluded that SCOF-CC has good potential with limited technological hinders for realization [66,69,70]. Besides SCOF-CC a number of other oxy-fuel cycles using steam/water as working fluids have been proposed including the Graz cycle [71], and the Water cycle [72] developed by Clean Energy Systems (CES). These cycles may require high temperature turbines and new design for the turbomachinery. For oxy-fuel gas turbine cycles, researches have been focused on thermodynamic studies of

system performance. The combustion behavior, e.g. the flame dynamics and reaction zone structures in the gas turbine combustors, is less addressed. From thermodynamic studies it has been shown that a small amount of trace species in the combustion products can have a great impact on the CO₂ capture, storage and transportation. Li et al. [73] demonstrated that the purification process of the flue gas stream of oxy-fuel combustion is highly influenced by the existence of impurities such as the small amount of N₂ resulted from the air separation units and the remaining O₂ in the flue gas due to incomplete combustion. The presence of non-condensable gases results in increased condensation duty for the recovery of the CO₂. This in turn leads to lower system efficiency and increased cost for separation. To minimize the oxygen concentration in the flue gas and meanwhile achieve complete combustion of fuel, stoichiometric mixture is preferred in oxy-fuel combustion. CO₂ and/or steam are used to control the flue gas temperature. Jericha and Gottlich [74] outlined a burner and combustor configuration, in which fuel, oxygen and steam were supplied separately in different inlets. The steam was supplied through an annular outer swirler inlet to form a swirling flow motion to wrap the flames and to cool down the flue gases.

Such combustor configuration would likely generate rather high flame temperature locally in the reaction zones that will enhance the dissociation of H₂O and CO₂ and thus affect the composition of the flue gas such that the un-consumed oxygen can be high in the flue gas. To reduce the flame temperature and thereby the remaining oxygen in the flue gas it can be beneficial to premix the oxygen and CO₂ or steam before injecting them to the combustor. There are several possibilities that need to be explored for example,

different levels of premixing of the fuel/oxygen /steam/CO₂ prior to their injection into the combustor, and different mixing patterns inside the combustor. The thermodynamic studies will give the same answer for the flue gas in the post flame zone if the inlet temperature, combustor pressure and the overall mass flows of fuel, oxygen, steam, and CO₂ streams are kept the same. However, the flame dynamics and reaction zone structures are dependent on combustor configurations as they are dictated by the detailed inflow conditions for the fuel/oxygen/steam and CO₂ supplies.

Optimal supply of oxygen and diluent to oxy-fuel combustion. To generate stable combustion in gas turbine combustion chambers with oxy-fuel combustion, certain minimal oxygen level in the oxidizer or elevated oxidizer temperature has to be maintained. The fundamental reason for this is the need to have sufficiently high temperature in the reaction zones for the chain reactions to proceed. Flame instability and poor burnout have been experienced when oxygen/CO₂ are premixed and supplied together to the flame as the oxidizer [75]. For example, in the recent experiments of Heil et al. [76] it was shown that poor burnout and lifted dark flames appeared when the oxygen mole fraction in the O₂/CO₂ stream was set to 21%; when the oxygen volume fraction was increased to 27% and 34%, full burnout and stable flames were obtained. In order to burn the fuel with lower oxygen level in the oxidizer (O₂/CO₂) stream the burner had to be modified to allow for recirculation of hot gases to the flame [76]. To improve the recirculation, the inlet design of the oxidizer mixture should be modified in order to mix the hot burned gases in the flame zone with the incoming fresh cold gases in order to stabilize the flame.



**Figure 2.4 Scheme of an air separation unit based on high temperature membranes
(exemplary flue gas swept) [90].**

In the study done by Kutne et.al.[77], the burner considered was a modified version of a practical gas turbine combustor with an air blast nozzle for liquid fuels [78]. Co-swirling oxidizer mixture was supplied to the flame through a central nozzle and an annular nozzle. The radial swirlers consisted of 8 channels for the central nozzle and 12 channels for the annular nozzle. The overall flow field of the flames is characterized by a conically shaped inflow of fresh gas, an inner recirculation zone (IRZ) and outer recirculation zone (ORZ) as sketched in Fig.2.5. In the shear layer formed between the inflow and the IRZ, the mixing of hot combustion products with fresh gas leads to a continuous ignition and stabilization of the flame. Same idea of conically shaped inlet for the oxidizer mixture is applied by our research group to our running system of gas turbine model combustor in order to improve the mixing process and so stabilizing the flame. However, it was found by our research group that the aspect ratio between the diameter of the inlet nozzle and the combustor diameter is playing an important role in calculating the amount of the oxidizer mixture that will be available for combustion and the amount that will escape between the flame zone and the reactor walls.

With high level oxygen in the oxidizer, the combustion products become hot and this may lead to high level of oxygen in the flue gas due to the dissociation reactions at high temperatures. There is an optimal “window” of oxygen/ diluent ratio in the oxidizer stream [79]. In the work done by Liu et al. [79], they reported that the primary oxidizer which is supplied in the upstream through the dome of the combustion chamber should have minimal oxygen level of 24% under the oxidizer temperature 520 K condition. The excessive CO₂ shall be supplied through the liner holes downstream of the primary

reaction zones to have a suitable temperature when the flue gas enters to the turbines. This will cool down the combustion products generated in the primary reaction zones. Stable combustion and low turbine inlet temperature can be obtained simultaneously by optimizing the oxygen and CO₂ supplies to the combustion chamber.

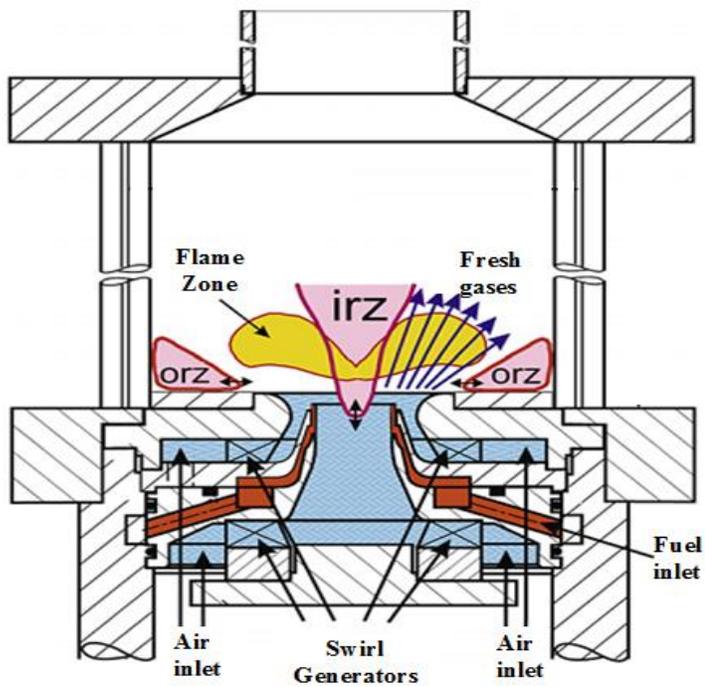


Figure 2.5 Schematic diagram of the combustion chamber used in the study of

Kutne et al. [77].

The stability of swirl stabilized oxyfuel/CH₄ flames was studied in the work done by Peter Kutne et al. [77] for O₂ mole fractions of 20– 40%, equivalence ratios of $\Phi=0.5-1$ and thermal powers of 10–30 kW. However, attempts of operating the burner with < 22% O₂ were unsuccessful even with conditions of $\Phi=1$ at 20 and 30 kW resulting in unstable operation and blow out.

Reactions characteristics. The oxyfuel combustion of coal in a steam turbine process is regarded as a possible way to use the oxyfuel process for CO₂ reduction. Research on this field is very active with the outcome that the first demonstration plants are in operation, and the power generation industry is willing to invest in this technology. Another way of particular interest is the use of oxyfuel combustion in gas turbines. This process offers the possibility to use the same post combustion techniques as for the oxyfuel coal process, in combination with an efficient combined cycle process [77]. Swirl flames are used extensively in practical combustion systems because they enable high energy conversion in a small volume and exhibit good ignition and stabilization behavior over a wide operating range [80-83]. In stationary gas turbine (GT) combustors, they are used mostly as premixed or partially premixed flames, and in aero engines, as diffusion flames. To reduce pollutant emissions, especially NO_x, today the flames are operated generally very lean [84-86]. Under these conditions, the flames tend to exhibit undesired instabilities, e.g., in the form of unsteady flame stabilization or thermoacoustic oscillations. The underlying mechanisms of the instabilities are based on the complex interaction between flow field, pressure, mixing, and chemical reactions, and are not well enough understood to date. Detailed measurements in full-scale combustors are hardly possible, and very

expensive and numerical tools have not yet reached a sufficient level of confidence to solve the problems. A promising strategy lies therefore in the establishment of a laboratory-scale “standard combustor” with practical relevance and detailed, comprehensive measurements using nonintrusive techniques with high accuracy. The gained data set will be used for validation and optimization of numerical combustion simulation codes which then can be applied to simulate the behavior of technical combustors. Intrusive probe measurements are less suited for these applications as they disturb the local flow field and change the conditions for stabilization and for reaction—locally or even in general [87,88]. In turbulent reacting flows, the use of optical measurement techniques is therefore essential for reliable information. Laser-based tools are the method of choice offering the potential to measure most of the important quantities with high temporal and spatial resolution, often as one- or two-dimensional images, and the ability to perform the simultaneous detection of several quantities [89-92].

In recent years a variety of laser-based investigations in GT model combustors have been reported that, besides feasibility studies, concentrated on certain aspects of the combustion process or model validation. For example, Kaaling et al. [93] performed temperature measurements with CARS in a RQL (rich-quench-lean) combustor, and Kampmann et al.[94] used CARS simultaneously with 2-D Rayleigh scattering to characterize the temperature distribution in a double-cone burner. In the same combustor, Dinkelacker et al. [95] studied the flame front structures and flame lift. Their experiments have been conducted at bluff-body-stabilized premixed methane/air flames, where flow and flame parameters have been varied systematically over a broad range of exit

velocities and stoichiometries. They found that for this burner configuration not only one but two different liftoff criteria must be met. For very lean mixtures the chemically dominated ignition delay is found to be the rate-determining step. For other cases, the liftoff height can be determined by a newly described turbulent mixing dominated model [95]. Fink et al. [96] investigated the influence of pressure on the combustion process by applying PLIF of OH and NO in a LPP (lean pre-evaporized premixed) model combustor. With respect to NO_x reduction strategies, Cooper and Laurendeau [97,98] performed quantitative NO LIF measurements in a lean direct injection spray flame at elevated pressures. They have performed excitation scans and calibration comparisons to assess the background contribution for PLIF detection. Also, they presented and analyzed quantitative radial NO profiles measured by LIF so as to correct the PLIF measurements to within the accuracy bars of the LIF measurements via a single-point scaling of the PLIF image. Shih et al. [99] applied PLIF of OH and seeded acetone in a lean premixed GT model combustor, and Deguchi et al. [100] used PLIF of OH and NO in a large practical GT combustor. They found that the automated LIBS unit is capable of monitoring trace element concentration fluctuations at ppb levels with a 1 min detection time under actual plant conditions. In addition, real-time measurement of O₂ and CO concentrations in a commercial incinerator furnace was performed using TDLAS to improve the combustion control. They reported also, using the multiple-point laser measurement results to control secondary air allocation, higher secondary combustion efficiency was achieved, and CO concentration was reduced. Hedman and Warren [101] used PLIF of OH, CARS, and LDV for the characterization of a GT-like combustor fired with propane in order to achieve a better understanding of the fundamentals of GT

combustion. PLIF of OH was also applied by Lee et al. [102] to study flame structures and instabilities in a lean premixed GT combustor, by Arnold et al. [103] to visualize flame fronts in a GT combustor flame of 400 kW, and by Fritz et al. [104] for revealing details of flashback. Lofstrom et al. [105] performed a feasibility study of two-photon LIF of CO and 2-D temperature mapping by LIF of seeded indium in a low-emission GT combustor. Four different laser diagnostic techniques were investigated in their work. The two more mature techniques, Planar Mie Scattering/Laser Induced Fluorescence and Planar Laser Induced Fluorescence of OH were used for fuel- and OH- visualisation, respectively. In addition, the applicability of some novel techniques in harsh industrial environments were investigated, two-line atomic fluorescence (TLAF) to obtain 2-dimensional temperature distributions, and two-photon LIF for the detection of CO. A comparison of two different laser excitation schemes for major species concentration measurements with laser Raman scattering was performed by Gittins et al. [106] in a GT combustion simulator. At a high-pressure test rig of the DLR, various laser techniques (LDV, CARS, PLIF of OH and kerosene, and 2-D temperature imaging via OH PLIF) were applied to GT combustors under technical operating conditions to achieve a better understanding of combustor behavior and to validate CFD codes [107-110].

Williams et al.[111] investigated syngas and methane flames for premixed swirl stabilized conditions for two different oxidizers of air and $O_2/CO_2/N_2$. Simple flame images for different conditions have been presented along with exhaust gas emissions. They report lower nitrogen oxides concentrations (NO_x) for the quasi-oxyfuel flames and higher carbon monoxide concentrations (CO), suggesting stoichiometric operation at 20–

24% O₂ as ideal for low emissions. Sautet et al. [112] studied the length of natural gas/oxygen diffusion flames in a jet burner for free and confined configurations. Fuel jet Reynolds numbers were varied from 8362 to 16300 for five flames of which two were buoyancy controlled. The flame lengths were calculated from OH-chemiluminescence and indicated flames to be 2–3 times shorter than air flames with adiabatic flame temperatures in the region of 3050 K. Ditaranto and Hals [113] discussed the effect of stoichiometric operation and high O₂ content in oxidizer on thermo-acoustic oscillations in sudden expansion jet configuration. They reported occurrence of thermo-acoustic instabilities as O₂ content in the oxidizer was increased, characterizing different instability modes dependant on flow velocity and flame speed variations.

2.3.2 Utilization of membrane reactor technology

In this review, we are focusing on oxy-fuel combustion using ion transport membranes in order to separate oxygen from air then this oxygen that permeates through the membrane is used in the combustion process in the other side of the membrane as shown in Fig.2.6. More recently, strong demand for tonnage quantities of oxygen is encouraged by the steady growth in chemical process operations. For instance, oxyfuel combustion process and oxygen-blown gasification to convert coal and natural gas into an intermediate synthesis gas that can be further processed to produce electricity, chemicals and transportation fuels [63]. There have been two fundamental approaches to air separation, which are cryogenic and non-cryogenic distillation. The cryogenic distillation is typically reserved for applications that require tonnage quantity of oxygen at ultra-low

temperature. The latter involves the separation of air at ambient temperatures using either molecular sieve adsorbents via pressure swing adsorption (PSA), or membrane separation process using the polymeric membranes. Recently, a third category of air separation has emerged, which is based on specialized ceramic membranes that separate oxygen from air at elevated temperatures, in contrast to the super-cooled temperatures required by conventional cryogenic distillation. This novel technique is based on dense ceramic membranes, which carry out the separation of oxygen from air at elevated temperatures, typically 800 to 900 °C. MIEC (Mixed Ionic Electronic Conducting) membranes, ITM (Ion Transport Membranes), and OTM (Oxygen Transport Membranes) are acronyms that used to refer to high temperature ceramic membranes [115]. These terms will be used throughout this work.

2.3.2.1 Concept of operation of ceramic based membranes

Ceramic based membranes for oxygen separation systems can be categorized into pure oxygen conducting membranes and mixed ionic–electronic conducting membranes. The solid electrolytes are pure oxygen conducting membranes, where electrodes are provided for the electron pathway [116]. The main advantage of this system is the control over the amount of oxygen generated via the application of an electric current. Compared to solid electrolytes, mixed ionic–electronic conducting membranes require neither electrodes nor an external circuit to operate. The electronic conductivity itself performs as an internal short circuit involving oxygen partial pressure gradient. Oxygen ions permeate from the high oxygen partial pressure side to the low oxygen partial pressure side, whilst the

overall charge neutrality is maintained by a counterbalancing flux of electrons, as idealized schematically in Fig.2.7. It should be noted that oxygen separation through this process has the advantage of producing high-purity oxygen.

It is worth noticing that ceramic materials with mixed ionic– electronic conducting characteristics typically have defined phase structures that can be derived from perovskite, fluorite, brownmillerite, and other similar types of materials [117-120]. Among ceramic membranes with mixed ionic–electronic conducting characteristics, perovskite-type and fluorite-type are the best structures in case of oxygen permeation properties; however, the perovskite type ceramic membranes have higher permeability and promising potential for improvement [121,122,137].

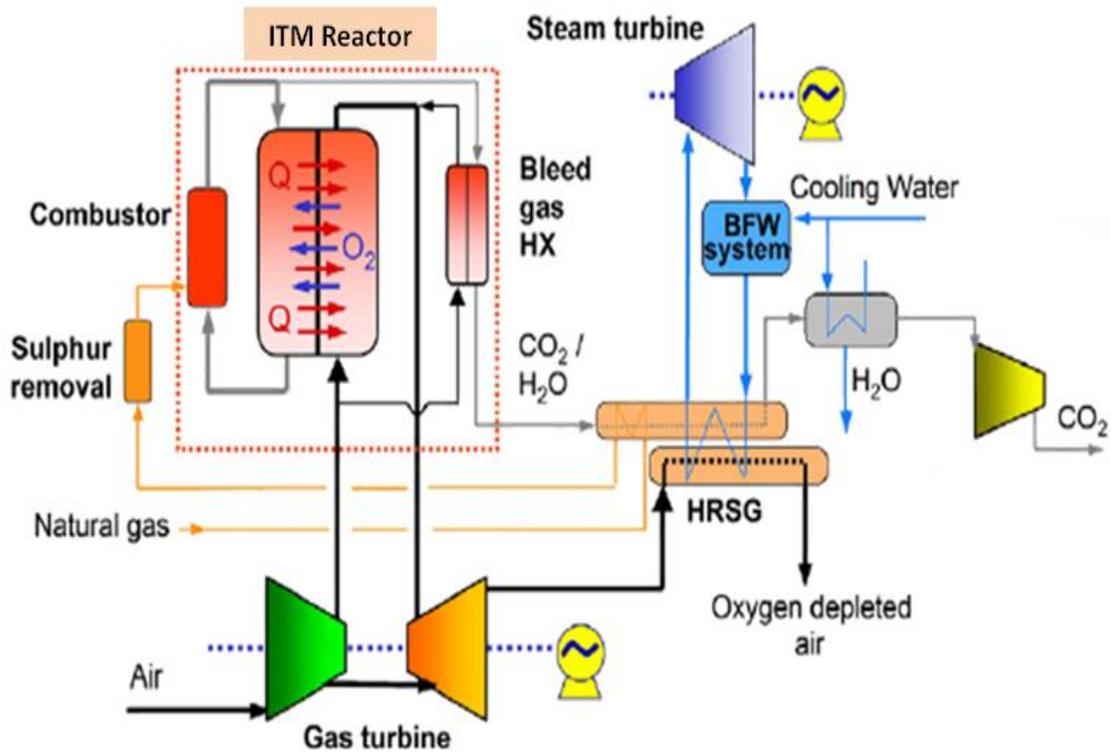


Figure 2.6 Illustrative flowsheet for oxy-fuel combustion process using membrane reactor technology, with additional unit operations for carbon capture [114].

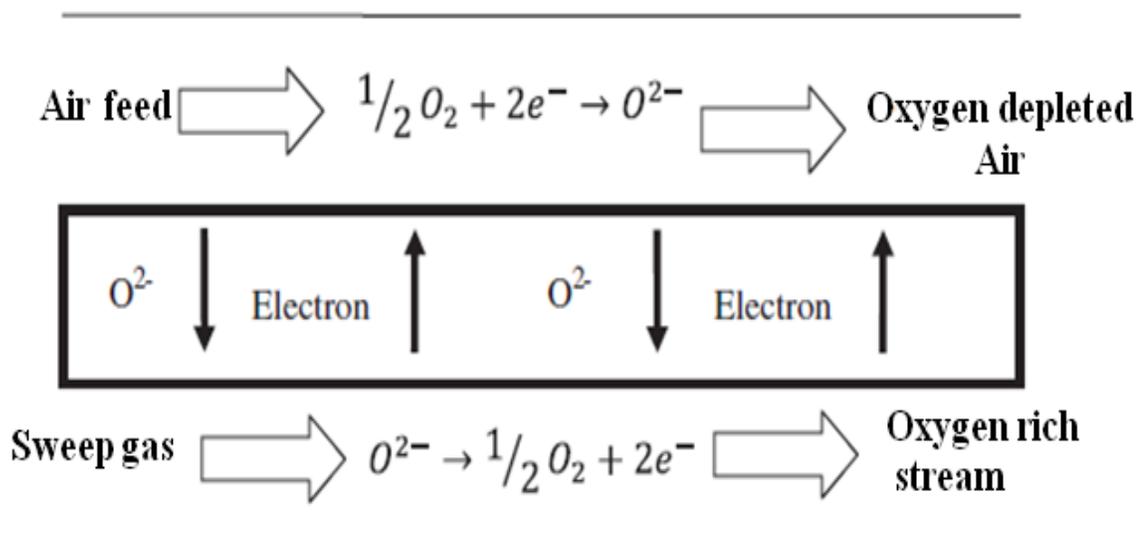


Figure 2.7 Schematic diagram of a dense ceramic membrane based on conduction mechanism.

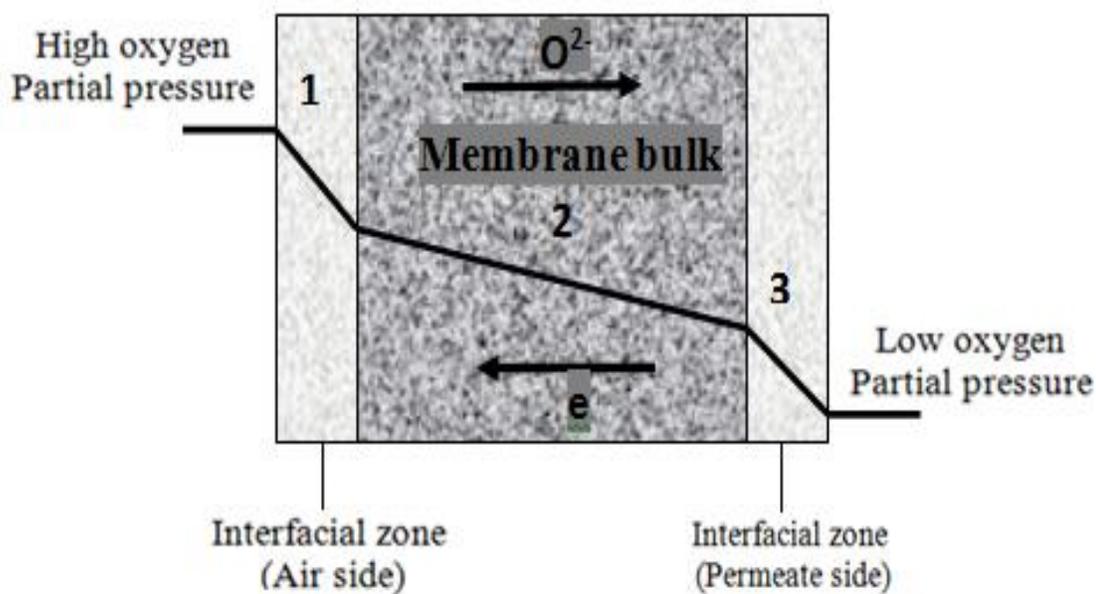


Figure 2.8 Schematic diagram of oxygen permeation through mixed ionic-conducting membrane [116].

2.3.2.2 Oxygen Transport mechanism

Based on the difference in the oxygen chemical potentials between the feed side and the permeate side, the membrane temperature and its ambipolar conductivity, oxygen migrates from the high pressure feed side to the low pressure permeate side, according to the overall transport processes summarized as follows [123-126]:

- i) gaseous oxygen mass transfer (advection and diffusion) from the feed stream to the membrane surface, adsorption onto the membrane surface, dissociation and ionization of oxygen molecules and subsequent incorporation of the ions into the lattice vacancies (feed side surface exchange),
- ii) Transport of lattice oxygen ions through the membrane (bulk diffusion),
- iii) Association of lattice oxygen ions to oxygen molecules and desorption from the membrane surface into the gas phase (permeate side surface exchange), gaseous oxygen mass transfer (advection and diffusion) from the membrane surface to the permeate stream. As we can see from Fig.2.8, Oxygen permeation through a dense mixed ionic–electronic conducting material is limited by surface exchange resistance, bulk diffusion limitations, or both [127-129]. It should be noted that the bulk diffusion will be the controlling step when the membrane is relatively thick.

Figure 2.8 visualizes the mechanism for oxygen permeation through a mixed ionic–electronic conducting membrane. It can be seen that the permeation process from the high oxygen partial pressure side to the low oxygen partial pressure side by dividing the

process into three zones: (1) an interfacial zone on the high partial pressure or air side; (2) a Central bulk zone; and (3) an interfacial zone on the low oxygen partial pressure or sweep gas side. The demonstration of incorporating both bulk diffusion and surface exchange kinetics into a single unambiguous equation has been done by few research groups [130-132]. For example, the following general assumptions were used for the derivation of Eq. (2.1) by Tan and Li [132] in the formation of mathematical models for the perovskite systems: 1) the oxygen permeation flux is controlled by the surface exchange reactions. 2) The operation is under steady-state isothermal operation. 3) The radial diffusion of gases is neglected. 4) Ideal gas law is applied to the gas phase. 5) The mass transfer resistance of gas phase to oxygen permeation is negligible and the oxygen partial pressures on both shell side and tube side of the membrane surfaces are the same.

$$\frac{dN_{O_2}}{dl} = \frac{K_f \left[(P'_{O_2})^{0.5} - (P''_{O_2})^{0.5} \right]}{\frac{K_f \ln(r_2 / r_1) (P'_{O_2})^{0.5} (P''_{O_2})^{0.5}}{\pi D_v} + \frac{(P'_{O_2})^{0.5}}{2\pi r_1} + \frac{(P''_{O_2})^{0.5}}{2\pi r_2}} \quad (2.1)$$

where N is the molar flow rate, l is the variable length of hollow fiber membrane, k_f is the forward reaction rate constant, D_v is the oxygen vacancy diffusion coefficient, p'_{O_2} and p''_{O_2} are partial pressures of oxygen at the feed and permeate side, respectively and r_2 and r_1 are the outer and inner diameter radius of the membrane tube.

Eq. (2.1) is specially derived for tubular membranes and has been applied successfully in the hollow-fiber systems of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [130] and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [138]. The detailed derivation of Eq. (2.1) can be found elsewhere [133-135]. The use of Eq. (2.1) for the perovskite systems is very useful in the

scaled-up engineering calculations, wherein the oxygen permeation flux performance inside the hollow-fiber perovskite membrane modules, which consists of many small-long tubes, can be estimated. Consequently, the oxygen permeation flux with respect to log mean membrane area, $dA_m = 2\pi r_m dl$ where $r_m = (r_2 - r_1) / \ln(r_2 / r_1)$ can be expressed by:

$$J_{O_2} = \frac{K_f D_v \left((P'_{O_2})^{0.5} - (P''_{O_2})^{0.5} \right)}{2(r_2 - r_1) K_f (P'_{O_2} P''_{O_2})^{0.5} + \frac{r_m}{r_1} D_v (P'_{O_2})^{0.5} + \frac{r_m}{r_1} D_v (P''_{O_2})^{0.5}} \quad (2.2)$$

For the sake of analyses, it is assumed that the oxygen permeation in Eq. (2.2) is still applicable to other mixed conducting membranes such as $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ [136] and $La_{0.2}Ba_{0.8}Co_{0.8}Fe_{0.2-x}Zr_xO_{3-\delta}$ [119]. L_c is defined by the membrane thickness at which the oxygen permeation resistance by bulk diffusion equals by the surface exchange reactions. L_c is expressed as:

$$L_c = \frac{D_v}{2K_f} \left(\frac{1}{P'_{O_2}{}^{0.5}} + \frac{1}{P''_{O_2}{}^{0.5}} \right) \quad (2.3)$$

It is noted in Eq.(2.3) that value depends on oxygen partial pressure and temperature. A larger characteristic thickness is resulted from higher and operating at lower temperature or lower oxygen partial pressure. When the membrane has a thickness far less than the critical thickness, L_c , the resistance by bulk diffusion can be neglected; therefore, the surface exchange reaction becomes the rate-limiting step. Lee et al. [138] indicated that the permeation in membranes in the thickness range of 1 to 2.6 mm was controlled both by the bulk diffusion of oxide ions and by surface exchange. In this case, Eq.(2.1) can be further simplified as [146]:

$$\frac{dNo_2}{dl} = \frac{K_f \left[(P'_{o_2})^{0.5} - (P''_{o_2})^{0.5} \right]}{\frac{(P'_{o_2})^{0.5}}{2\pi r_1} + \frac{(P''_{o_2})^{0.5}}{2\pi r_2}} \quad (2.4)$$

Surface exchange reactions may involve many sub-steps, which are oxygen transfer from the gas phase to membrane phase, physical adsorption on surface, dissociation with electronic transfer to yield chemisorbed oxygen species, and the incorporation in surface layer including the reverse reactions [139].

The oxygen permeation flux is inversely proportional to the membrane thickness; thus, reducing the membrane thickness will increase the oxygen permeation as long as bulk diffusion prevails. Kim et al. [128] derived an equation applicable in tubular perovskite membranes to explain the oxygen permeation data in $Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ in the surface exchange reaction limited. Eq. (2.5) can be used for surface exchange limited region in tubular perovskite membranes.

$$J_{o_2} = \frac{\pi r_1 r_2 k}{(r_1 + r_2) S} \left(\frac{\sqrt{P'_{o_2}}}{\sqrt{P^o_{o_2}}} - \frac{\sqrt{P''_{o_2}}}{\sqrt{P^o_{o_2}}} \right) \quad (2.5)$$

where, k is the surface exchange coefficient unit and S is the effective membrane area. When a membrane is relatively thick, the overall oxygen permeation is controlled by the bulk diffusion. The flux in this case is generally described by Wagner theory [134]. The flux of oxygen, J_{o_2} is given by Eq. (2.6):

$$J_{o_2} = \frac{1}{4^2 F^2 L} \int_{\mu_{o_2}^{(2)}}^{\mu_{o_2}^{(1)}} t_i t_e \sigma_t d\mu_{o_2} \quad (2.6)$$

where F (C/ mol) the Faraday constant; L (m) the membrane thickness and t is the

product of the electronic transference number t_e , ionic transference number t_i and total conductivity σ_t . Lin et al. [141] and Qi et al. [142] derived the oxygen permeation flux equations for ionic or mixed-conducting ceramic membranes in terms of electrical conductivity. In this case, the oxygen permeation flux can be expressed as:

$$J_{O_2} = \frac{RT}{4F^2L} \left[\sigma_h(P'_{O_2}) \left(1 - \left(\frac{P''_{O_2}}{P'_{O_2}} \right)^{1/4} \right) + \sigma_e(P'_{O_2}) \left(\left(\frac{P''_{O_2}}{P'_{O_2}} \right)^{1/4} - 1 \right) \right] \quad (2.7)$$

where, R (J/mol K) is the gas constant and T (K) is the temperature. Eq. (2.7) has been used successfully by Rui et al. [144] to describe the oxygen permeation through dense ceramic membranes with finite rate of chemical reaction. Oxygen permeation flux within $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.3}\text{O}_{3-\delta}$ (t = 1.2 mm, T = 873–953 K) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (t = 1.12 mm, T = 1273 K) is well explained by this equation. Although Eq. (2.7) is originally an empirical equation, it has been applied in the literature [145] with reasonable predictions.

Wang et al. [134] revealed that the controlling step of the oxygen permeation for the 1.5 mm thickness BSCF tubular membrane was bulk diffusion at the temperature range of 700 °C to 900 °C; hence, the surface exchange reaction does not favor the oxygen permeation flux. The oxygen permeation flux is described in Eq. (2.8).

$$J_{O_2} = \frac{\pi L C_i D_a}{2S \ln(r_1/r_2)} \ln \left(\frac{P''_{O_2}}{P'_{O_2}} \right) \quad (2.8)$$

where C_i stands for density of oxygen ions and D_a for ambipolar oxygen ion-hole diffusion coefficient. D_a could be determined from oxygen permeation flux data. Ge et al.

[135] theoretically analyzed that the oxygen permeation flux through $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ disk-shaped membrane at 950 °C was controlled by both the bulk diffusion and oxygen surface exchange reactions; therefore, the oxygen permeation flux is given as:

$$J_{O_2} = \frac{D_v}{2L} \frac{\frac{K_f}{\frac{1}{(P'_{O_2})^{0.5}} + \frac{1}{(P''_{O_2})^{0.5}}}}{\frac{1}{(P'_{O_2})^{0.5}} + \frac{1}{(P''_{O_2})^{0.5}} + \frac{D_v}{2L}} (C^{e_v} - C^{e_v}) \quad (2.9)$$

Where C^e and $C^{e'}$ are the oxygen vacancy concentrations in the material under thermal equilibrium with the atmosphere surrounded by oxygen partial pressure at feed side and oxygen partial pressure at the permeate side and (P'_{O_2} and P''_{O_2}), respectively. D_v and k_f can be determined by proper fitting of the experimental data into Eq. (2.9), which requires prior knowledge of (a) C^e and $C^{e'}$ values and (b) the oxygen permeation fluxes under the applied oxygen partial pressure gradient across the membrane at selected temperatures by oxygen permeation experiments [135].

Chang et al. [140] systematically compared the performance of symmetric (1.5 mm thick) and asymmetric mixed-conducting membranes (200 μm -thick thin dense layer and 1.3 mm-thick support) with correlation of overall oxygen permeation resistance across the membrane. They prepared the asymmetric membrane consists of the support and thin dense layer from the same composition $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ (SCFZ) perovskite-type oxide. The oxygen permeation flux in both membrane architectures is represented as:

$$J_{O_2} = \frac{1}{S} \frac{RT}{R_p + R_d} \ln \left(\frac{P'_{O_2}}{P''_{O_2}} \right) \quad (2.10)$$

Where R_p and R_d are the resistance in the porous support and thin dense layer, respectively. For an asymmetric membrane, the overall resistance is the sum of the resistance in the porous support and in the thin dense layer ($R_{\text{overall}} = R_p + R_d$). In the symmetric membrane $R_{\text{overall}} = R_p$. They concluded that the oxygen permeation flux on the asymmetric membrane was higher than the symmetric membrane due to the significant decrease of bulk diffusion resistance in the thin dense layer of the asymmetric membrane. Chang et al. [140] reported detailed calculation of the overall oxygen permeation resistance and modeling of the transport resistance through a membrane.

2.3.2.3 Membrane permeation characteristics

The performance of oxygen permeation flux depends on both membrane materials and the membrane thickness. The permeation conditions such as pressure and temperature also influence the flux according to the Eq.(2.7); in addition, the sweep gas flow rate also plays an important role. The dependence of oxygen permeation flux on the thickness of the disk membrane of 0.55, 1.10 and 1.65 mm has been observed by Sunarso et al. [147]. As can be seen in Fig.2.9, the oxygen permeation flux was insignificant when the temperature was lower than 600 °C; however, at temperature higher than 650 °C, considerable oxygen permeation flux value was obtained. These researchers claimed that the sharp increase of oxygen permeation flux was obtained when the temperature was above 800 °C due to the improvement of oxygen ionic diffusion and/or surface reaction rate. It can be obviously seen the six fold enhancement (from 0.2 to 1.2 ml/ cm²min) for

0.55 mm disk membrane thickness when the temperature increased from 800 to 950 °C. Sunarso et al. [147] also revealed that the oxygen permeation flux increased as the membrane thickness decreased, especially when the temperature was higher than 800 °C. Interestingly, they observed that the increase of oxygen permeation flux was not inversely proportional to the membrane thickness reduction. This can be explained by reducing the thickness of the disk membrane by half, which was from 1.10 mm to 0.55 mm; as a result, the increase of oxygen permeation fluxes was only 20%, rather than 100%. From the results obtained, Sunarso et al. [147] suggested that both bulk diffusion and surface exchange kinetics were the rate limiting steps for the oxygen transport across the membranes. The similar observation was reported by Watanabe et al. [148].

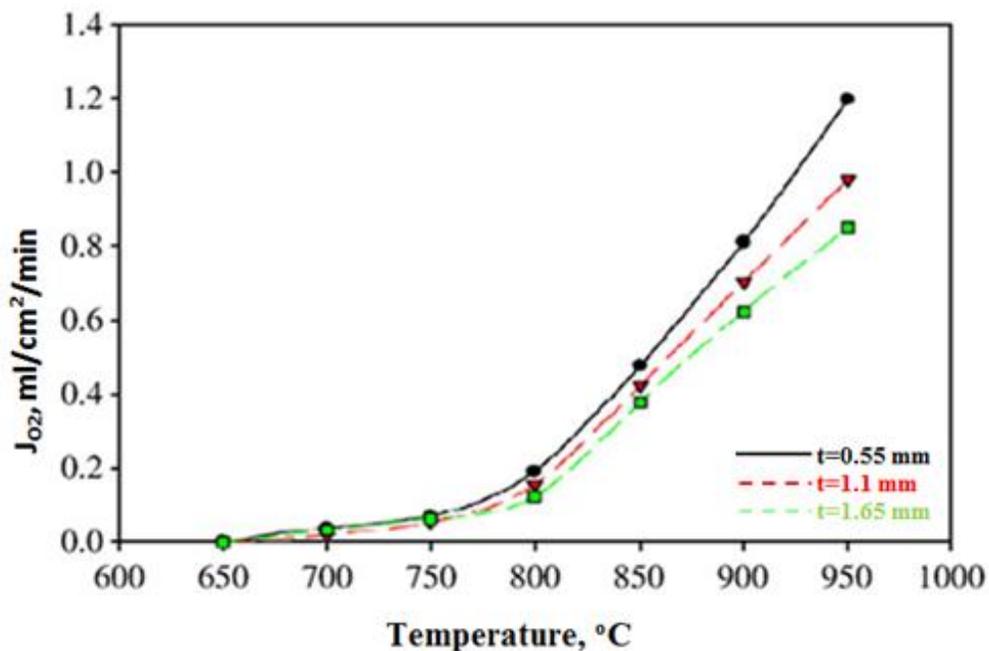


Figure 2.9 Oxygen permeation fluxes as function of temperature at different membrane thickness [147].

Zhu et al. [149] investigated the performance of oxygen permeation flux of dense $\text{BaCe}_{0.15}\text{Fe}_{0.85}\text{O}_{3-\delta}$ (BCF1585) ceramic membranes synthesized by the solid-state reaction (SSR) method and EDTA-citric acid (EC) method. Fig.2.10 shows the dependence of oxygen permeation flux of BCF1585 membranes synthesized by different methods on the operating temperatures. Fig.2.10 shows the oxygen permeation flux of the membrane synthesized by SSR method was higher than the membrane synthesized by EC method. They observed the oxygen permeation flux for the SSR method derived membrane was $0.92 \text{ ml/ cm}^2\cdot\text{min}$ compared to EC method derived membrane with $0.71 \text{ ml/ cm}^2\cdot\text{min}$ at $940 \text{ }^\circ\text{C}$, respectively. It has been reported by Han et al. [150] that oxygen partial pressure in the permeate side could reach as low as 10^{-13} atm . under the vacuum operation model; as a result, the oxygen permeation flux would be extremely high. It is vitally important to note that the mechanical strength of thinner perovskite membranes under such condition is very poor; therefore, the deposition of a thin membrane on a porous support or asymmetric structure seems to be a wise solution.

Li and Tan [132] found that the LSCF hollow-fiber module operated at elevated pressure may not be a good choice compared to the operation under vacuum conditions. They observed that the oxygen flux of $0.31 \text{ ml/cm}_2\cdot\text{min}$ can be obtained when the vacuum pressure in the tube side of the module is reduced to 0.01 atm . additionally; they claimed that it would not be possible to achieve such oxygen permeation flux at elevated pressure operation even the shell side pressure is increased to 30 atm . It can be noted that the elevated pressure operation is generally adopted in the conventional polymeric hollow-fiber membrane modules for gas separation. Therefore, the vacuum operation in the

permeate side of the membrane is more preferable. In addition, Li and Tan [132] claimed that the improvement in oxygen flux can be observed when the pressure in the permeate side is decreased, but only up to a certain pressure value or effective pressure. The enhancement in level improves the performance in oxygen permeation flux because the driving force across the membrane is increased. However, there is no improvement in oxygen permeation flux with further decrease in the vacuum.

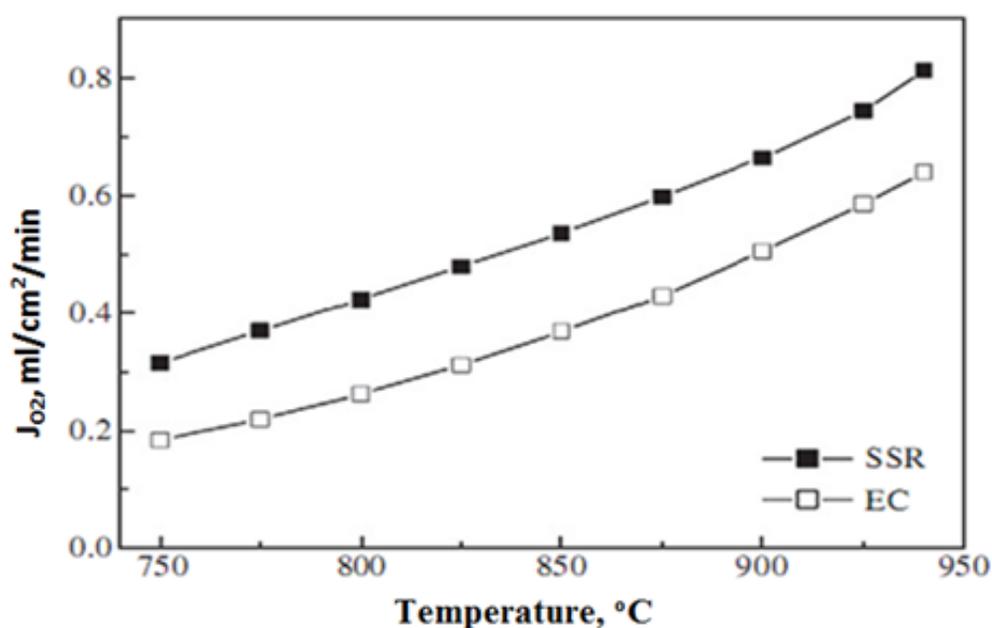


Figure 2.10 Dependence of oxygen permeation flux of the membranes synthesized by different methods on temperature [149].

Zydorczak et al. [151] studied the performance of oxygen permeation flux in an ultra-thin $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ by investigating the effects of operating temperatures and sweep gas flow rate (helium) on the oxygen permeation fluxes. They observed that the oxygen permeation flux increased when the operating temperature was increased. The similar trend occurs with the increasing of sweep gas flow rates. The oxygen partial pressure difference across the hollow fiber membrane is increased when flow rate of sweep gas increased. The oxygen partial pressure gradient acts as the driving force for the transport of oxygen through the membrane; therefore, the sharp increase in oxygen permeation flux can be observed. The reduced membrane thickness does contribute to the improved oxygen permeation flux, than that reported in previous studies by Tan et al. [152] and Wang et al. [153]. It is important to note that surface exchange reaction and bulk diffusion are two factors that contribute to the transport resistance with respect to the operating temperature. Surface exchange reaction is the rate limiting step at lower temperatures; conversely, bulk diffusion becomes the rate limiting step with the increase in the temperature. The similar observation has been reported by Xu and Thomson [130]. The hollow fiber membrane developed is extremely thin; hence, at high temperature, the flux will increase rapidly. They concluded that the reduced thickness of the membrane has an enormous effect on oxygen permeation flux as the ionic bulk diffusion will be the rate limiting step at high temperature.

Another study done by Tan and Li [154] revealed the effect of sweep gas operation to the performance of oxygen permeation flux in hollow fiber modules. They observed that the oxygen concentration in the permeate side decreased when the argon flow rate is

increased for all the operating temperatures. They reported that the use of water vapor as a sweep gas in investigating the oxygen flux gave the same operating performance as under argon gas condition. Wang et al. [155] investigated the production of high-purity oxygen by BCFZ perovskite hollow fiber membranes swept with steam; consequently, they found that the oxygen permeation obtained was $4.1 \text{ ml/cm}^2\text{min}$ at $875 \text{ }^\circ\text{C}$. Hence, they concluded that the steam employed as a sweep gas has a promising potential to produce high-purity oxygen with reasonable oxygen permeation flux due to the problems related to high temperature sealing can be solved. However, two fundamental problems of employing steam or water vapor are membrane stability and membrane module itself. Tan et al. [154] and Wang et al. [155] did not explain these two problems due to the limitation of experimental apparatus.

2.3.2.4 Oxygen permeation with chemical reactions

Mixed ionic and electronic conducting ceramic membranes have received increasing interest from academia and industry. A major industrial effort is currently devoted to the development of the mixed-conducting ceramic membrane reactor technology for combustion of hydrocarbons.

Permeation equation. In the ceramic membrane reactor, oxygen permeates through the ionic or mixed-conducting ceramic membrane via a complex mechanism. It usually includes adsorption of oxygen and charge transfer reaction on the membrane surface exposed to air, oxygen vacancy and electron diffusion in the membrane bulk, and charge

transfer and chemical reaction on the membrane surface exposed to a reducing gas. The detailed mathematical formulation for oxygen permeation through mixed-conducting ceramic membranes is fairly complex [141]. The oxygen permeation through oxygen ionic or mixed-conducting ceramic membranes under reaction conditions was also examined by Zebao et. al. [156] with a model taking into account of different electrical transport mechanisms (p-type and n-type transports) and finite reaction rate. It was demonstrated in their work that with a reaction consuming oxygen in one side of the membrane, the oxygen partial pressure in the reaction side decreases and the oxygen permeation flux increases with the increase in the reaction rate for both the p-type and the n-type transport dominated mechanism. Also they reported that the increase in reaction rate causes a transition of the transport mechanism from p-type to n-type. This transition leads to an increase in the permeation flux by up to 30 times. This effect offers one explanation for the large discrepancies in published permeation data for membrane reactors of partial oxidation reaction employing an oxygen permeable dense ceramic membrane [156]. They reported also, for a membrane with a specific transport mechanism, the increase in the reactant partial pressure causes an increase in the reaction rate and oxygen permeation flux. However, the increase in the inlet inert gas amount has a complicated effect on the oxygen permeation flux because it lowers both oxygen partial pressure and the reaction rate at the same time.

The OCM (oxidative coupling of methane) and SOE (selective oxidation of ethane) reactions involve oxidative reactions of methane or ethane to form ethylene as the intermediate (desired) product. The final (equilibrium) product is carbon dioxide (and water). Both the OCM and SOE reaction mechanisms are very complex and may involve over hundreds of steps [143,157]. Akin and Jerry [158] demonstrated how the extent of the reaction (or reactivity) and reactant flow rate affect the oxygen permeation flux, they used the following simple reaction to exemplify the complex oxidative reactions of methane or ethane to ethylene and finally to carbon dioxide:



Where, carbon monoxide represents a hydrocarbon reactant. The use of this simple reaction can help in obtaining semi-analytical solution for the combustion with oxygen permeation. The basic principle illustrated with this simple reaction can be extended for the more complex reaction systems if detailed reaction mechanism and kinetic equations are known. In order to obtain analytical expressions for the oxygen partial pressure in the reaction chamber, Akin and Jerry [158] used a simple reactor model, continuously stirred tank reactor (CSTR), to describe the reaction chamber in this work. Since in most laboratory studies, membrane reactor experiments were conducted on disk-shaped or short tubular membrane, such as the BYS used in their work, the CSTR model can catch the major characteristics of the oxidation reaction in the membrane reaction chamber. Instead of putting specific reaction kinetics in the model in account for reaction rate, they only considered two extreme cases in the modeling and analysis: (a) extremely fast reaction rate, i.e., complete conversion of the reactant (CO in this work) with oxygen permeating to the reaction chamber, (b) extremely slow reaction rate, i.e., no reaction

between the oxygen permeating with the reactant (CO). In the second case, the reactant fed into the reaction side behaves like an inert gas, such as the case of oxygen permeation experiments with helium as purge. The real case would lie between these two extreme cases. Oxygen permeation flux through dense ionic or mixed conducting ceramic membranes can be related to air and reaction side oxygen partial pressures, as proposed in their model [158]. For ionic or mixed-conductors with ionic transference number close to 1 and electron conduction dominated by the transport of the electron-holes (such as yttria-stabilized zirconia and doped bismuth oxide) [159-161], the oxygen permeation flux can be approximated by the following equation:

$$J_{O_2} = k(P'_{O_2}{}^{1/n} - P''_{O_2}{}^{1/n}) \quad (2.11)$$

Note in this case the driving force is the oxygen partial pressure in the air side minus the oxygen partial pressure in the reaction side with a positive value for constant n (i.e., $n > 0$). For convenience in notation, this group of membranes with oxygen permeation equation in the form of Eq. (2.11) is referred to in this paper as membranes with p-type flux equation.

For ionic conductors with electron conduction dominated by the electrons, such as yttria doped zirconia at low oxygen partial pressure range [162], or for mixed conductors with ionic transference number close to zero, such as lanthanum cobaltite, the permeation flux equation can be expressed by

$$J_{O_2} = k(P''_{O_2}{}^{1/n} - P'_{O_2}{}^{1/n}) \quad (2.12)$$

Note in this case the driving force is the oxygen partial pressure in the reaction side minus the oxygen partial pressure in the air side with a negative value for constant n ($n < 1$). For convenience in notation, these groups of membranes are referred to here as membranes with n -type flux equation. Table 2.1 summarizes the parameters used in their study. The values for constants, k and n in Eq. (2.11), for a membrane with p -type flux equation are chosen for the bismuth-based oxide $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BYS) [163]. The k and n values for a membrane with n -type flux equation in Eq. (2.12) are calculated from the literature oxygen permeation data given for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) [130]. As proposed by Xu and Thomason [130], The concentration of oxygen vacancies at both surfaces of the membrane (C'_v and C''_v) is also governed by surface exchange kinetics for the following two surface reactions (forward reaction in the feed side and backward reaction in the permeate side):



where O^x represents lattice oxygen in the perovskite crystal structure, k_f and k_r are, respectively, the forward and reverse reaction rate constants for the forward reaction (or the reverse and forward rate constants for backward reaction). It should be noted that because of the high electronic conductivity, the electron holes are essentially constant at both surfaces of the membrane, and thus the reverse reaction rate of Reaction B and the forward reaction rate of Reaction C are pseudo zero-order at steady state under isothermal conditions. According to this, they have correlated the steady-state oxygen permeation flux as a function of P'_{O_2} , P''_{O_2} and membrane temperature and thickness:

$$J_{O_2} = \frac{D_V K_r (P'_{O_2}{}^{0.5} - P''_{O_2}{}^{0.5})}{2LK_f (P'_{O_2} P''_{O_2})^{0.5} + D_V (P'_{O_2}{}^{0.5} + P''_{O_2}{}^{0.5})} \quad (2.13)$$

Where D_V , K_r and K_f are functions of temperature and the specific properties of the membrane. The values of those parameters have been determined by our research group by fitting the experimental oxygen flux data in the work done by kusaba et al. [163] as a function of temperatures as shown in Fig.2.11. As shown in the figure, both the experimental data and our present Dkk model (D_V , K_r and K_f model) are in a very good agreement. Also, the as the temperature of the membrane surface increases as the oxygen permeation flux across the membrane increases due to the reduced surface resistance of the membrane as a result of temperature increase. The fitted values of the coefficients D_V , K_r and K_f are listed in table 2.2 and also the values of the activation energies.

A semi-empirical form found in the literature also was used extensively to determine the local oxygen flux as a function of the membrane Temperature, the feed and permeate oxygen partial pressures, and empirical constants that depend on the specific material. This form allows for interchangeable oxygen flux mechanisms to be implemented quickly and effectively within the model in order to explore the impact of different ITM membrane materials [116].

$$J_{O_2} = A * \exp(-B/T_M) * (P'_{O_2}{}^n - P''_{O_2}{}^n) \quad (2.14)$$

The pre-exponential A in some sense accounts mostly for the diffusion coefficient and the membrane thickness dependence, while B represents the effective activation energy

or Arrhenius dependence due to both surface exchange kinetics and diffusion coefficient activation energy. This mechanism is chosen because it is simple, relatively accurate with respect to experimental data, and reasonably captures the impact of both surface exchange kinetics as well as the temperature dependence of the oxygen vacancy diffusion coefficient. However, it is limited in the sense that it applies for a specific membrane thickness, and also cannot be extrapolated too far from the experimental conditions used to obtain the fitted values for A and B [116]. The functional dependence on partial pressure is assumed to be $n=0.5$ for LSCF, and $n=0.25$ for LNO based on global surface exchange kinetics theory and experimental results and the values of A and B are $26.75 \text{ mol m}^{-2} \text{ s}^{-1} \text{ pa}^{-n}$, 16510 K for LSCF and $2.011 \text{ mol m}^{-2} \text{ s}^{-1} \text{ pa}^{-n}$, 10240 K for LNO respectively. This is consistent with the mixed control, i.e., both diffusion and surface kinetics, in contrast to diffusion dominant where n is typically less than zero [164].

Membrane reactor performance. Little work was reported with a focus on examining the effects of reaction side conditions on oxygen permeation through the mixed-conducting ceramic membranes. In membrane reactors for partial oxidation of a hydrocarbon, one side of the ionic or mixed-conducting ceramic membrane is exposed to air and the other side to a hydrocarbon gas. Oxygen from the air side permeates through the membrane and reacts with the hydrocarbon in the reaction side. Although it is generally agreed that the driving force for oxygen permeation is the oxygen potential gradient across the membrane, the oxygen partial pressure, or oxygen chemical potential in the reaction side is very difficult to define or measure by experiments [165]. As a result, the quantitative value of oxygen potential gradient across an ionic or mixed-

conducting ceramic membrane exposed to air and a hydrocarbon is not fixed. It is expected that the permeation flux through an ionic conducting ceramic membrane depends on many parameters in a membrane reactor.

TABLE 2.1 Summary of parameters used in the parametric study [158].

Parameter	Range
Q_{feed}^0 (ml/min)	100-675
T (°C)	850
A (cm ²)	1.8
k (ml/min cm ² atm ^{1/n})	
BYS (ml/min cm ² atm ^{1/n})	0.035
LSCF(ml/min cm ² atm ^{1/n})	0.16
<u>n</u>	
BYS	3.34
LSCF	-8.06

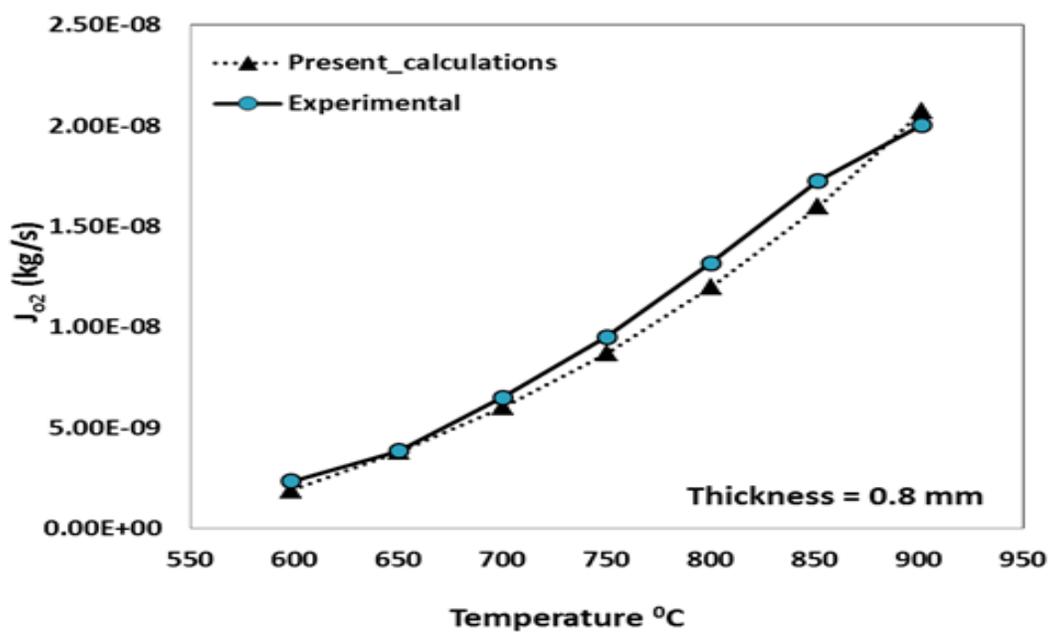


Figure 2.11 Fitting of the experimental data of Oxygen permeation through LSCF1991 membrane having a thickness of 0.8 mm [163] with our present permeation model.

TABLE 2.2 The obtained pre-exponential coefficients and activation energies of D_v , k_f and k_r for LSCF-1991 membrane from our work [170] through the fitting of experimental data of [163].

Expression	Pre-Exponential coefficients		Activation Energy (kJ/mol)
	Unit	Value	
$D_v = D_v^0 \exp(-E_D/RT)$	m^2/s	1.58×10^{-5}	73.6
$K_f = k_f^0 \exp(-E_f/RT)$	$m/atm^{0.5} \cdot s$	1.11×10^{10}	226.9
$K_r = k_r^0 \exp(-E_r/RT)$	$mol/m^2 \cdot s$	3.85×10^{11}	241.3

Akin and Jerry [158] presented a simple mathematical analysis, coupled with experimental data, on the effects of hydrocarbon flow rate and reactivity with oxygen on the oxygen permeation in an ionic or mixed conducting ceramic membrane reactor for partial oxidation of hydrocarbon. In their work, Oxygen permeation experiments were conducted on a fluorite structured $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BYS) membrane. The BYS is primarily an oxygen ionic conductor with a considerable electronic conductivity due to the doping of samarium. The membrane used in their work was a short BYS tubes, of 3–4cm in length and 4mm in inner diameter, were prepared from the citrate derived BYS powder followed by a green machining method [158]. Oxygen permeation experiments were conducted, respectively, with methane and ethane as the feed to the reaction side. Oxygen permeating through the BYS membrane reacted with methane or ethane, with main reaction being oxidative coupling of methane (OCM) in the former [139] and selective oxidation of ethane (SOE) to ethylene for the latter [157]. The BYS membrane surface is catalytically active for OCM and SOE. Furthermore, these reactions typically involve formation of a radical on membrane surface followed by a homogeneous reaction in the gas phase inside the membrane tube. Therefore, no other catalyst was packed to the tube side of the BYS membrane in these studies. Oxygen permeation through oxygen ionic or mixed-conducting ceramic membranes under reaction conditions was analyzed in their work by a simple mathematical model considering different transport mechanisms (with n-type versus p-type flux equations) and oxidation reaction kinetics (extremely fast reaction versus no reaction). Experimental oxygen permeation data for $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}$ (BYS) membrane under two different reaction conditions (with methane and ethane) were measured and analyzed by the modeling results.

They showed that for a membrane under reaction conditions with a specific reducing gas, the oxygen permeation flux depends strongly on the oxidation reaction rate and the reducing gas flow rate. Such dependencies are different for membranes with oxygen permeation controlled by p-type electron transport and those by n-type electron or oxygen vacancy transport. Also they reported that oxygen permeation flux under the condition of extremely fast reaction is several fold higher than that under the condition of slow reaction as a result of the decrease of the oxygen partial pressure in the reaction side with increasing reaction rate. Also they found that the oxygen permeation flux through BYS membrane under the reaction conditions with ethane is about one order of magnitude higher than that with methane because of the significantly faster oxidation reaction with ethane than with methane. The analysis results also suggest that increasing oxidation reaction rate in the reaction side by use of a heterogeneous catalyst can enhance the oxygen permeation flux through an ionic or mixed-conducting ceramic membrane. For a membrane with a fixed oxygen permeation mechanism, increasing gas flow rate lowers the conversion of oxidation reaction in the reaction side (equivalent to a decrease in reaction rate), causing a decrease in the oxygen permeation flux. Varying reactant flow rate may also cause a change in oxygen permeation mechanism leading to a complex permeation flux versus flow rate relationship [158].

These perovskite-type ionic conductors have technological applications in devices such as oxygen ion conducting solid electrodes, solid oxide fuel cells (SOFC), and electrochemical oxygen pumps (EOP) and oxygen sensors [166]. There is also a great potential to use these materials as a membrane in a catalytic reactor. In this case, oxygen is

separated from air and then used for selective oxidation reactions such as the oxidative coupling of methane (OCM) to (C_{2+}) higher hydrocarbons or methane partial oxidation to synthesis gas [167]. In a study using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF-6428) as the catalytic membrane for the OCM reaction, Xu and Thomson [168] found that the oxygen permeation rate was higher than that required for methane activation on the membrane surface. Consequently, excess oxygen ions recombined to form oxygen molecules, which caused serious combustion of methane in the gas phase and reduced the selectivity of the desired C_{2+} products. Moreover, in a separate study of the stability of these membranes [25], they showed that morphological changes on the methane side of the membrane surface caused significant changes in the oxygen permeation flux. The surface reaction rate was found to limit the CO oxidation rate in a $La_{1-y}Sr_yFeO_{3-\delta}$ ($Y=0.1,0.2$) membrane where the rate was nearly independent of the membrane thickness. Hence, in order to achieve practical and effective applications of these membrane reactors for partial oxidative reactions, it is essential to understand the oxygen permeation mechanism and to determine the rate limiting step among the processes of mass transfer, ionic transport, and surface reactions [130].

Xu and Thomson [130] developed an explicit oxygen permeation model in a stagnation flow for ion-conducting membranes with a high ratio of electronic to ionic conductivity, which makes it possible to correlate the permeation flux to directly measurable variables. Surface exchange kinetics at each side of the membrane was emphasized and their resistance to oxygen permeation has been quantitatively distinguished from the bulk diffusion resistance. They conducted a series of experimental measurements of oxygen

fluxes for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ over a wide range of temperature and oxygen partial pressures and they used the results for model regression purposes and for mechanism analysis. They concluded that the oxygen permeation at low temperatures (750 °C) is limited by the rate of oxygen-ion recombination but is dominantly controlled by bulk diffusion at high temperatures (950 °C) and this is consistent with activation energies for oxygen vacancy diffusion and for the surface exchange rates, which are estimated at 74 kJ/mol and 227, 241 kJ/mol, respectively.

In our recent study [169], the characteristics of oxyfuel combustion in an oxygen transport reactor (OTR) have been investigated. In this work, the cylindrical reactor walls were made of dense, nonporous, mixed-conducting ceramic membranes that only allow oxygen permeation from the outside air into the combustion chamber and the simulations have been done for different composition of CH_4/CO_2 mixtures and for different mass flow rates. The comparison between reactive and separation-only OTR units showed that combining reaction and separation increases significantly O_2 permeation rate to about 2.5 times under the assumptions given therein [169] and the results indicated that the heat of reaction is mostly transferred to the air side with a portion used to heat the O_2 permeating flux. For higher mass flow rates, the OTR operates with rich mixture resulting in low CH_4 conversion.

CHAPTER 3

EXPERIMENTAL SETUP AND NUMERICAL MODELING

OF THE GAS TURBINE MODEL COMBUSTOR

To satisfy this objective, experimental and numerical investigations on an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor are conducted. The other application is through the use of ion transport membrane (ITM) reactor technology. Also to satisfy this objective, numerical investigations are conducted in order to understand the oxygen permeation process and oxy-fuel combustion characteristics inside a 2D simple symmetric design ITM reactor. From our understandings that come out from the above 2D analysis of the simple symmetric design ITM reactor, a new 3D reactor design will be introduced for the substitution of ITM reactors into a gas turbine combustor. The total volume of the reactor and the total number of channels required will be decided according to the simulation results in order to give a power more close to that available through using real gas turbines.

3.1 Experimental setup

3.1.1 Combustor Design

Figure 3.1 shows a schematic drawing of the swirl stabilized gas turbine model combustor. The non-swirling fuel (CH_4) is supplied through 16 channels made on the round surface of a bluff body with diameter of 5 mm and are inserted at the top part of the fuel tube (1/4" outside diameter) in order to generate the required velocity to stabilize the flame. Each fuel channel has dimensions of 0.45 mm x 0.2 mm. The oxidizer (O_2/CO_2 mixture at room temperature) is supplied to the combustion chamber through an annular space between the fuel inlet pipe of 6.35 mm diameter and an outside diffuser which has inlet diameter, outlet diameters and length of 10 mm, 20 mm, and 5 mm respectively. The exit plane of the fuel channels is assigned to be the reference zero height of the flame ($h = 0$ mm) and the exit plane of the oxidizer is located below the fuel exit plane by a distance of 5 mm. The overall flow field of the flame is characterized by this conically shaped inflow of fresh gas. An outer recirculation zone has been created in the lower part of the reactor between the flame and the wall of the reactor and as a result, the mixing of hot combustion products with fresh gas leads to a continuous ignition and stabilization of the flame. The burner is mounted in an optically accessible combustion chamber which consists of a quartz tube of 12 inches height and 3 inches mm inside diameter.

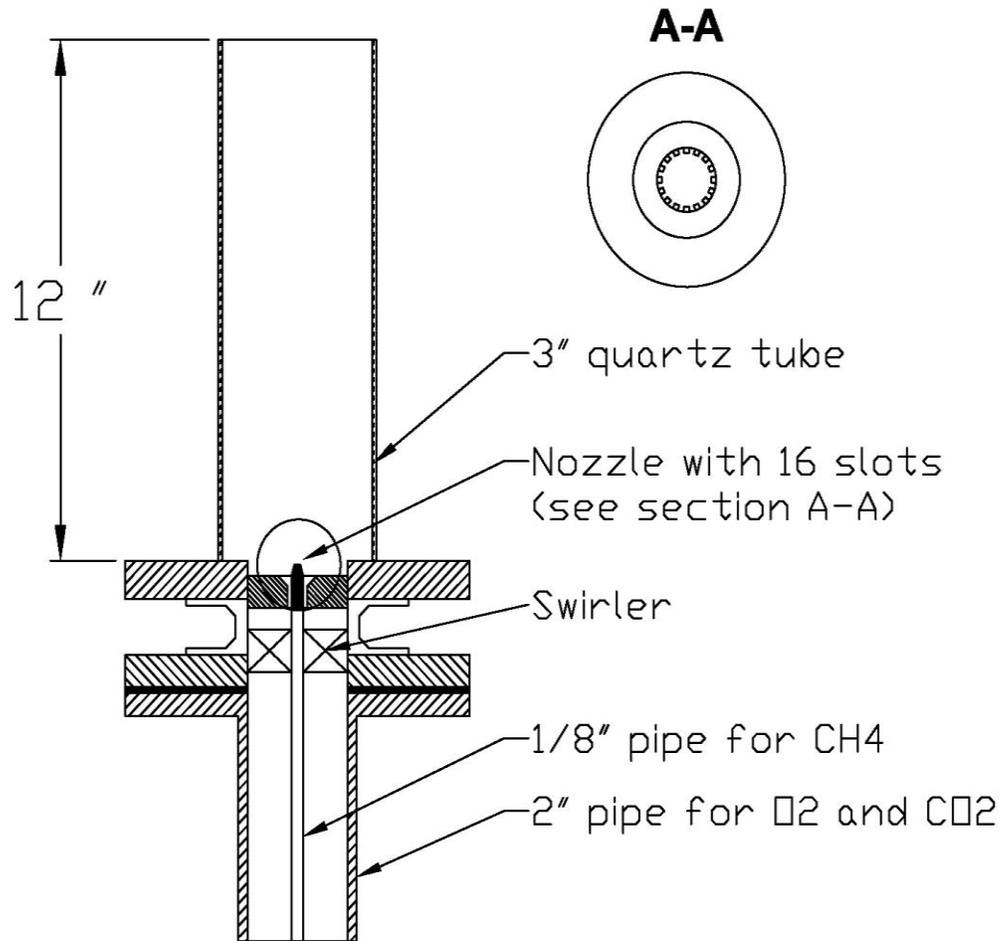


Figure 3.1 Schematic of the atmospheric pressure swirl stabilized gas turbine combustor.

The burner can provide power ranging from $4.1 \text{ MW/m}^3 \cdot \text{bar}$ at 6 L/min fuel volume flow rate up to $6.2 \text{ MW/m}^3 \cdot \text{bar}$ at 10 l/min fuel volume flow rate that is comparable to most industrial gas turbines, which are operated at 3.5 to $20 \text{ MW/m}^3 \cdot \text{bar}$. In order to shorten and stabilize the flame, a swirler with a swirl angle of 60 degrees is used to apply the required swirl for air. The swirler is located just below the oxidizer inlet to the reactor inside a supplying tube of 2 inches inside diameter as shown in Fig.3.1.

To generate high flow velocity at the exit section of the combustor to prevent the back flow from the surrounding to the reactor, a conically shaped top part made of steel with a minimum diameter at its top of 50 mm and a length of 100 mm is used to form the exhaust gas exit. This conical exhaust part is supported with holes to enable measuring both the inner reactor temperature and species concentrations.

3.1.2 Experimental facility

Figure 3.2 shows a schematic of the experimental test-rig facility used in this work. The oxygen and carbon dioxide oxidizer is premixed before injection into the combustor to reduce the flame temperature and thereby reducing the remaining oxygen in the flue gas. The oxygen is mixed with carbon dioxide upstream of the combustor in a mixing chamber (A) which has a cylindrical shape of 150 mm diameter, 300 mm length, and an internal throat of 50 mm diameter. The mixing chamber has three inlets for O_2 , CO_2 (for oxy-combustion experiments) and air and has one outlet. To improve the mixing of O_2 and CO_2 , the O_2/CO_2 mixture (feed gas) passes through a supply pipe (B) of 50.8 mm inside diameter upstream of the reactor and with a height of 1.2 m before the inlet to the

combustor at the top part as shown in Fig.3.2. Methane is supplied through a 6.4 mm (1/4") tube extended from the cylinder to the reactor inlet (C) and a bluff body containing slits on its surface forming the fuel channels to generate the required velocity of the fuel flow. All gases are supplied from compressed gas cylinders and the flow is controlled through pressure regulators and valves. To measure the flow rate, a flow rotameter is used in each gas line and the mass flow rate is controlled by a mass flow controller from Bronkhorest HIGH-TECH (D-type, model number F-201CI-10K-AGD-22-V for CH₄, F202AI-M20-AAD-55-V for O₂ and F-202AI-M20-AGD-55-V for CO₂, with uncertainty of $\pm 0.5\%$ of full scale). The controllers are connected to a computer for data logging and post processing.

The exhaust gas temperature is measured at the exit plan of the reactor (height of 300 mm) with R-type thermocouple from Omega which has a maximum range of 1500 °C and inserted inside a 12 inches long ceramic probe to protect it from high flame temperature. As the measurements have been recorded only at the exit section of the reactor, the size of the probes did not affect the operation of the flame. The thermocouple probe is connected to a data logger and a computer which takes the average temperature at each location during one minute. Similar local temperature measurements are repeated and average values are calculated at each location. The thermocouple probe enters the reactor from its top as shown in Fig.3.2 and a traverse mechanism is used to move the probe precisely in the axial and radial directions inside the reactor. For higher flame temperatures, a B-type thermocouple from Omega is used with the ability to measure the temperature up to 1950 °C. A high speed camera is used to visualize and compare different flames. The camera is fixed at the same level of the reactor.

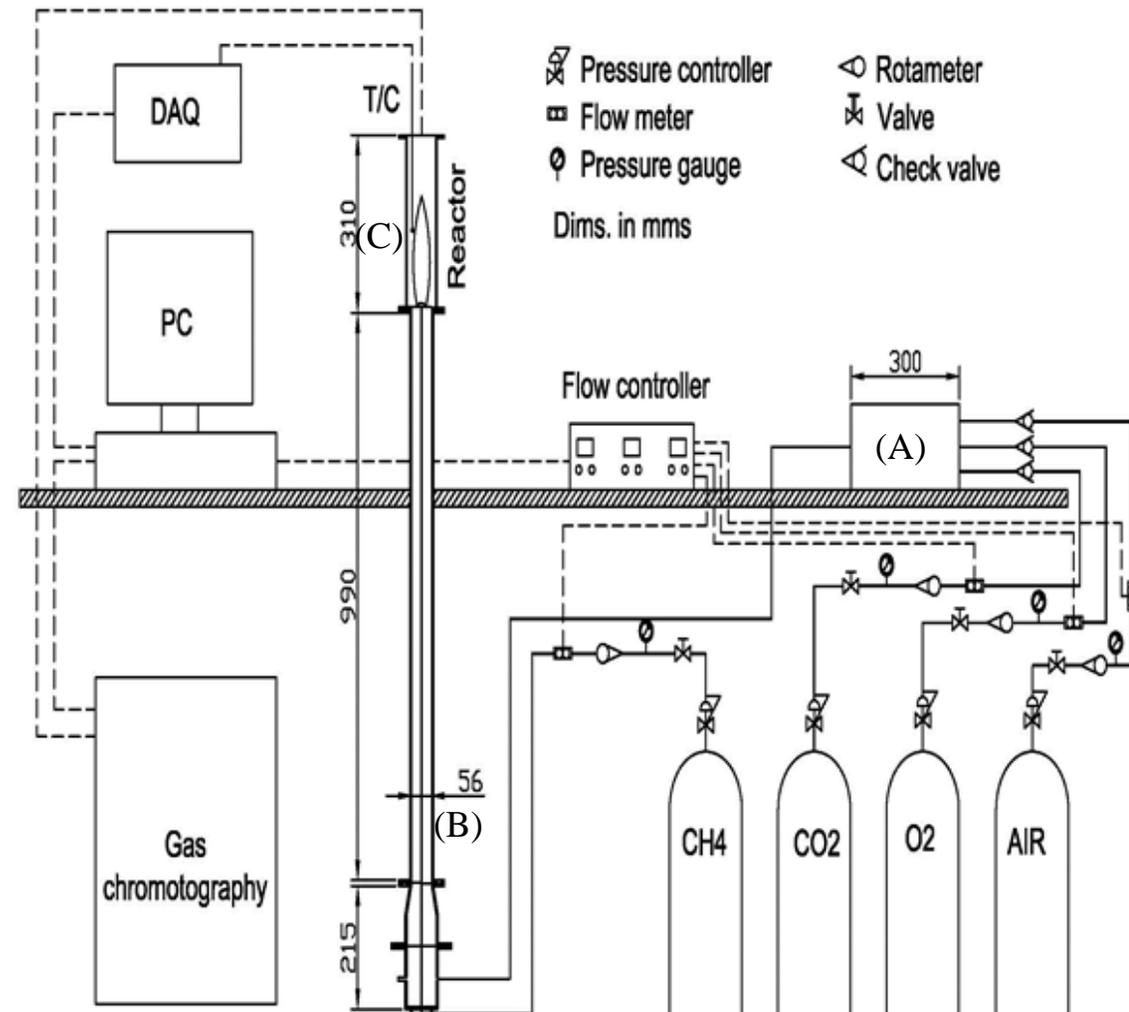


Figure 3.2 Schematic of the test-rig facility used for the present study.

Gas composition data consisting of O₂, CO, CO₂, dissolved N₂ and total unburned hydrocarbon (HC) concentrations were measured at the exit section of the combustor (h=300 mm) using a gas chromatography, model 450-G.C. The sample is supplied to the gas chromatograph through a suction fan after quenching it at the exit section using a specially designed probe to prevent reactions and protect the pump blades. The probe consists of three tubes, the sample is sucked through the inner tube (dia. of 1/8") and the cooling water is supplied in the annular area between the outer pipe (dia. of 0.5 inch) and the middle tube (dia. of 0.25 inch) and leaves from the annulus between the inner and the middle tubes. The flow of water is controlled in order to prevent the condensation inside the probe. The exit pipe of the fan is lengthy and has a sudden drop in diameter to complete the cooling process to separate H₂O before injecting the sample to the G.C. to introduce the sample as dry. The total hydrocarbon concentration is measured as methane equivalents by means of an FID (flame ionization detector) based instrument. The analysis of O₂, CO, N₂ and CO₂ were performed by a Thermal Conductivity Detector (TCD) which is the most universal detector available with different measurement ranges, adapted for reference and O₂/CO₂ conditions, respectively. The gas is dried and filtered before it is fed into the on-line gas analyzer train.

3.1.3 Operating conditions

Two sets of experiments are conducted with the first focusing on determining flame stability for equivalence ratios ranging from 0.5 to 1, fuel volume flow rates from 5 to 10 l/min and at different O₂ concentrations in the oxidizer ranging from 100 % O₂ (0 % CO₂) to the percent of O₂ that leads to blow out of the flame. The considered blends of the

oxidizer mixture of O₂/CO₂ are 100/0, 80/20, 60/40, 50/50, 40/60, 30/70 and 25/75 by volume. The conditions for the flame blow out are determined by reducing the percentage of O₂ from 25% by a step of 1% until blow out state is reached. The high speed camera is used to visualize the size, shape and position of the heat release zone. The second set of experiments involve measurements to characterize the flames by measuring the main species concentration at the exhaust section of the combustor, exhaust temperature, and inside reactor temperature profile through the flame from the bottom of the reactor to the exhaust section which can serve as a database for combustion models validation. The temperature at the exit section of the reactor is measured in the radial direction at radii of 0, 10, 20, 30 mm.. The fuel volume flow rate is changed for each equivalence ratio from 5 l/min to 10 l/min by a step of 1 l/min and at each value of fuel volume flow rate. Also, at a certain equivalence ratio; all the different percentages of O₂/CO₂ have been checked. All gases are introduced to the combustion chamber at atmospheric pressure and at a temperature of 22 °C.

The flames obtained in the present work are established under globally lean conditions which showed no soot production and burned with a light blue color. The flames also appeared with a conically shaped flame zone at all operating conditions. The width of the flame is increased through the combustor height to completely occupy the quartz reactor tube at a certain height. The flames are stabilized in this design by two recirculation zones. One recirculation zone is inside the flame itself due to the bluff body at the end of the fuel pipe which accelerates the fuel and cause a recirculation zone inside the flame. The second recirculation zone is created due to the existence of the conically shaped

oxidizer inlet which forms a recirculation zone near to the reactor wall. Flame visualization shows a good radial symmetry.

A simplified equation is used to calculate the swirl number as given in Eq. (3.1). The equation was simplified to eliminate the need for static pressure measurement and the final form is based on the velocity at reactor inlet just above the nozzle exit.

$$S = \frac{\int_0^{R_o} V_z W r^2 dr}{R_o \int_0^{R_o} V_z^2 r dr} \quad (3.1)$$

where, V_z is the axial velocity, W is the tangential velocity, and R_o is the radius of at the nozzle exit. The swirl number is calculated for the investigated cases of the present work and is found to have a range of 0.5 to 0.6. The nozzle is contoured and a combustion chamber is used with an expansion factor (D/d) of 3.5 where D is the inner diameter of combustion chamber and d is the diameter of the nozzle at the reactor inlet. Both inner and outer recirculation zones are expected to break down the vortex motion. The Reynolds number is calculated for each case based on the cold inflow conditions and a nozzle diameter of 10 mm. The mass flow rate is calculated at the standard temperature and pressure while the viscosity of the mixture is calculated using the correlation given by Warnatz et al. [171].

3.1.4 Uncertainty and error analysis

Errors and uncertainties in the measuring devices are very important parameters in the analysis of the experimental data. Those errors can rise from instrument selection, instrument condition, instrument calibration, environment and observation. This analysis of uncertainty is also important to prove the accuracy of the experiments. The uncertainty analysis is performed using the method described by Holman et al. [191]. In the present experiments, temperatures and flow rates are measured using appropriate instruments as described above. The total uncertainty of any measured parameter may be calculated as follows:

$$\omega_M = (\omega_{\text{sensor}}^2 + \omega_{\text{DAS}}^2 + \omega_{\text{Calib}}^2)^{1/2} \quad (3.2)$$

where, ω_M is the uncertainty in any measured parameter, M , ω_{sensor} is the uncertainty in the sensor reading, ω_{DAS} is the uncertainty associated with the data acquisition system and ω_{Cal} is the uncertainty in the calibration process. The uncertainties in the measured parameters are presented in Table 3.1. Reproducibility of results was checked by repeating a set of tests for two times under the same conditions and taking the average values.

TABLE 3.1 Uncertainty of the measured parameters.

Quantity	Exhaust Temperature	Gases mass flow rates
Uncertainty, %	±0.5 (°C)	±2 %

3.2 Numerical model setup

3.2.1 General Conservation equations

The mathematical model is based on the numerical solution of the conservation equations for mass, momentum, and energy, and transport equations for scalar variables. The equations, which are elliptic and three-dimensional, were solved to provide predictions of the flow pattern, thermal and emissions characteristics of reacting medium inside a gas turbine model combustor. The equations which govern the conservation of mass, momentum and energy as well as the equations for species transport may be expressed in the following general form [172]:

$$\frac{\partial}{\partial x_j} \left(\bar{\rho} \bar{U}_j \Phi + \bar{\rho} \bar{u}_j \phi \right) = \frac{\partial}{\partial x_j} \left[\Gamma_\phi \frac{\partial \Phi}{\partial x_j} \right] + \bar{\rho} S_\phi \quad (3.3)$$

where Φ and ϕ are the average and fluctuating values of the dependent variable and u_j is the velocity component along the coordinate direction x_j , $\bar{\rho}$ is the fluid density, Γ_ϕ is the diffusion coefficient and S_ϕ is the source term.

Equation (3.3) stands for the mass conservation equation when $\Phi = 1$; the momentum conservation equation when Φ is a velocity component; the energy equation when Φ is the stagnation enthalpy; or the transport equation of a scalar when Φ is a scalar variable such as mixture fraction.

3.2.2 Turbulence model

The present work utilizes the k- ε model of Versteeg and Malalasekera [173]. The Reynolds stresses and turbulent scalar fluxes are related to the gradients of the mean velocities and scalar variable, respectively, via exchange coefficients as follows:

$$-\overline{\rho u_i u_j} = \mu_t \left(\frac{\partial \bar{U}_i}{\partial x_j} + \frac{\partial \bar{U}_j}{\partial x_i} \right) - \frac{2}{3} \rho k \delta_{ij} \quad (3.4)$$

$$-\overline{\rho u_j \phi} = \Gamma_\phi \frac{\partial \Phi}{\partial x_j} \quad (3.5)$$

where: μ_t is the turbulent viscosity and Γ_ϕ is equal to μ_t / σ_ϕ . The turbulent viscosity is modeled as:

$$\mu_t = c_\mu \rho k^2 / \varepsilon \quad (3.6)$$

Where: c_μ and σ_ϕ are constants. The turbulent viscosity is thus obtained from the solution of the transport equations for k and ε . RNG (Renormalized group) turbulence model [174] was used to provide better results for vertical flows.

The eddy dissipation model that described turbulence-chemistry interaction in non-premixed combustion was utilized in the present work to provide the production rate of species. The conservation equations of the kinetic energy of turbulence and The rate of dissipation of the kinetic energy of turbulence are [175]:

$$\frac{\partial}{\partial x_j} (\rho \bar{U}_j k) = \frac{\partial}{\partial x_j} \left(\frac{\mu_{eff}}{\sigma_k} \frac{\partial k}{\partial x_i} \right) + G_k - \rho \varepsilon \quad (3.7)$$

$$\frac{\partial}{\partial x_j} (\rho \bar{U}_j \varepsilon) = \frac{\partial}{\partial x_i} \left(\frac{\mu_{eff}}{\sigma_\varepsilon} \frac{\partial \varepsilon}{\partial x_i} \right) + C_1 G_k \frac{\varepsilon}{k} - C_2^* \rho \frac{\varepsilon^2}{k} \quad (3.8)$$

where G_k represents the generation of turbulent kinetic energy due to the mean velocity gradients and is given by:

$$G_k = -\rho \overline{u_i u_j} \frac{\partial \bar{U}_j}{\partial x_i} \quad (3.9)$$

The quantities σ_k and σ_ε are the effective Prandtl numbers for k and ε , respectively and C_2^* is given as:

$$C_2^* = C_2 + C_3 \quad (3.10)$$

where C_3 is a function of the term k/ε and, therefore, the model is responsive to the effects of rapid strain and streamline curvature and is suitable for the present calculations.

The model constants C_1 and C_2 have the values; $C_1=1.42$ and $C_2 =1.68$. The wall functions establish the link between the field variables at the near-wall cells and the corresponding quantities at the wall.

3.2.3 Radiation model

The solution of the radiative transfer equation (RTE) was obtained using the discrete ordinates (DO) radiation model. The RTE equation is written as:

$$\frac{dI(\mathbf{r}, \mathbf{s})}{ds} = \kappa I_b - (\kappa + \sigma_s) I(r, s) \quad (3.11)$$

The total radiation intensity I , depends on the position vector, r , and the path length s . κ is the absorption coefficient and σ_s is the scattering coefficient. The Planck mean absorption coefficient is given as:

$$\kappa_p(T, P) = \frac{\int_0^{\infty} \kappa_{\lambda}(\lambda, T, P) e_{b\lambda}(\lambda, T) d\lambda}{\sigma T^4} \quad (3.12)$$

where $e_{b\lambda}$ is the blackbody spectral emissive power. The blackbody spectral emissive power is calculated using variables by Zheng et al. [176].

3.2.4 Species Transport Equations

The mass fraction of each species m_l , is predicted through the solution of a convection-diffusion equation for the l^{th} species. The present calculations utilize a modified two-step methane-oxycombustion reaction kinetics model as described below which solves the transport equations for the species of O₂, CO₂, CO and H₂O. The conservation equations can be expressed in the following form:

$$\frac{\partial}{\partial x_i} (\rho \bar{U}_i m_l) = -\frac{\partial}{\partial x_i} J_{l,i} + R_l \quad (3.13)$$

where R_l is the mass rate of creation or depletion by chemical reaction of the species l , $J_{l,i}$ is the diffusion flux of species l , which arises due to concentration gradients which is given by:

$$J_{l,i} = -\left(\rho D_{l,m} + \frac{\mu_t}{Sc_t}\right) \frac{\partial m_l}{\partial x_i} \quad (3.14)$$

where $D_{l,m}$ is the diffusion coefficient for species l in the mixture and Sc_t is the turbulent Schmidt number, $\frac{\mu_t}{\rho D_t}$ is equal to 0.7.

An eddy-dissipation model [177] that relates the rate of reaction to the rate of dissipation of the reactant- and product-containing eddies is used to calculate the rate of reaction.

The source of chemical species i due to reaction, R_i , is computed as the sum of the reaction sources over the N_R reactions, thus:

$$R_i = M_i \sum_{k=1}^{N_R} R_{i,k} \quad (3.15)$$

where M_i is the molecular weight of species i and $R_{i,k}$ is the molar rate of creation/destruction of species i in reaction k . The reaction rate, $R_{i,k}$ is controlled either by an Arrhenius kinetic rate expression or by the mixing of the turbulent eddies containing fluctuating species concentrations. The rate of reaction $R_{i,k}$ is given by the smaller value of the two expressions below:

$$R_{i,k} = \nu_{i,k} M_i A \rho \frac{\varepsilon}{k} \frac{m_R}{\nu_{R,k} M_R} \quad (3.16)$$

$$R_{i,k} = \nu_{i,k} M_i A B \rho \frac{\varepsilon}{k} \frac{\sum_p m_p}{\sum_j \nu_{j,k} M_j} \quad (3.16)$$

where m_p is the mass fraction of a product species (P), m_R is the mass fraction of a reactant (R), where R is the reactant species giving the smallest value of $R_{i,k}$, A is an empirical constant equal to 4.0, B is an empirical constant equal to 0.5, $\nu_{R,k}$ is the stoichiometric coefficient for reactant i in reaction k and $\nu_{j,k}$ is the stoichiometric coefficient for product i in reaction k . The eddy-dissipation model relates the rate of reaction to the rate of dissipation of the reactant- and product-containing eddies and the term k/ε represents the time scale of the turbulent eddies.

3.2.5 Reaction kinetics model

As a matter of fact, numerical modeling of combustion applications is a computationally demanding process. That's why it is necessary to apply simplified reaction mechanisms to reduce the computing cost. Examples of CFD modeling in combustion application using the global mechanisms are found in the literature [178,179]. However, computationally simple mechanisms are cheap, simple and available; the simplified schemes cannot be expected to give accurate results especially under oxy-fuel combustion conditions. The replacement of inert N₂ with a chemically reactive compound, CO₂, has been shown to change the importance of some of the elementary reactions governing the combustion, thereby requiring a modification of the global multistep reaction mechanisms to make them valid under oxy-fuel conditions [180].

In the present work, the two-step hydrocarbon oxidation mechanism by Westbrook and Dryer [181] which was modified by Andersen et al. [29] is used for the calculations of the reaction kinetics, since this scheme is directly available as default in the commercial CFD code Fluent. The model was modified to handle the increased CO₂ concentration under oxy-fuel conditions. The Westbrook and Dryer model [181] consists of two reactions, where the last step, oxidation of CO to CO₂, is reversible. The mechanism is listed in the form of three irreversible steps:



For this model, the modified reactions rates data by Andersen et.al. [29] are listed in Table 3.2. The set of governing equations and boundary conditions are solved numerically. The details of the calculation procedure can be found in previous works [172, 182]. Gambit 2.2 was used to construct the mesh and as the reactor is symmetric as shown in Fig.3.1, only half part of the reactor was modeled with a mesh of more than 5,00,000 finite volumes was used with very small boundary control volumes in the regions of high gradients. The CFD code Fluent 12.1 was selected for the solution of the steady-state conservation equations.

TABLE 3.2 Modified two-Step Methane-oxygen Combustion Mechanisms with Kinetic Rate Data.[29].

Reaction number	Reactions	A	β	E_a (J/kmole)	Reaction orders
Reaction 1	$\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$	1.59×10^{13}	0	1.998×10^8	$[\text{CH}_4]^{0.7} [\text{O}_2]^{0.8}$
Reaction 2	$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	3.98×10^8	0	4.18×10^7	$[\text{CO}] [\text{O}_2]^{0.25} [\text{H}_2\text{O}]^{0.5}$
Reaction 3	$\text{CO}_2 \rightarrow \text{CO} + 0.5\text{O}_2$	6.16×10^{13}	-0.97	3.277×10^8	$[\text{CO}_2] [\text{H}_2\text{O}]^{0.5} [\text{O}_2]^{-0.25}$

CHAPTER 4

NUMERICAL MODELING OF THE ITM REACTORS

4.1 2D membrane reactor model setup

4.1.1 2D reactor specifications and operating conditions

In this work, the membrane reactor model shown in Fig.4.1 is used as the ITM reactor. As shown in the figure, an LSCF-1991 ionic ceramic membrane separates an oxygen containing upstream (typically air) and a downstream containing the sweep gases. The geometry of reactor was selected to facilitate comparison with numerical work and to reduce spatial variations to two dimensions. Due to the symmetry in the reactor design, only half of the domain is considered as the symmetry plane is passing through the middle of the membrane surface area.

The sweep gas tested in the present work is a mixture of CH_4+CO_2 for the analysis of the membrane reactor application. More details about membrane specifications are listed in table 4.1. The surface area of the membrane is 8cm X 8cm and it has an operating temperature range of 700 °C to 950°C [163]. The normal distance to the membrane surface, L, between fuel inlet and the membrane surface is varied, in this study, from 15mm to 90 mm in order to investigate the effect of reactor geometry on the permeation

and combustion process. The temperature of both streams in the feed and permeate sides of the membrane is varied between 700 °C and 1000 °C to see its effect also.

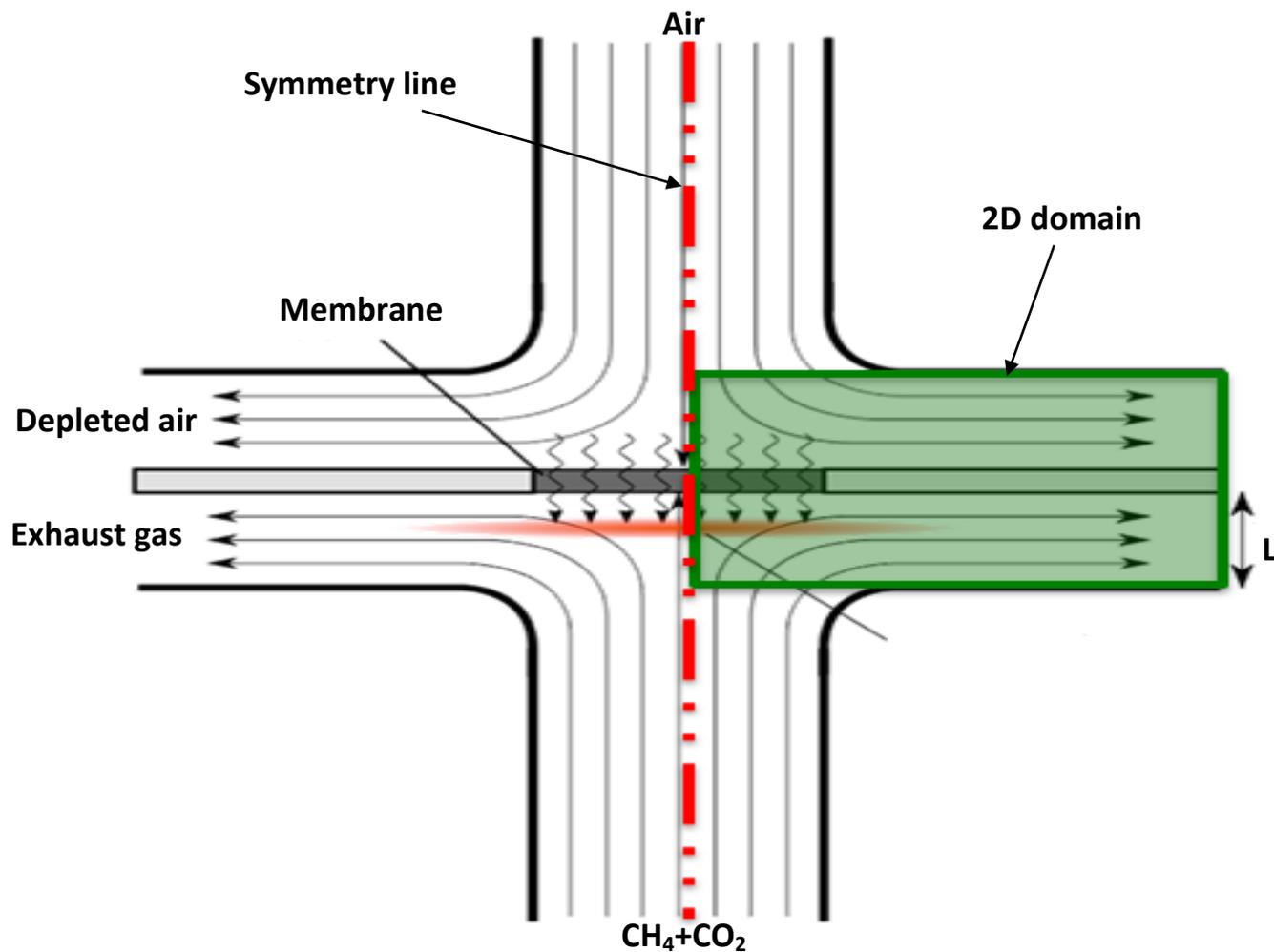


Figure 4.1 Schematic diagram of the 2D representation of the membrane reactor used in the CFD model.

Both sides of the reactor are maintained at atmospheric pressure. The simulations were carried out over a wide range of volume flow rates of both feed and permeate flows (100, to 2000 standard cubic centimeter per minute, sccm). The pre-exponential coefficients of the Dkk (D_v , K_f and K_r coefficients model) oxygen flux permeation equation model have been fitted using the available experimental data in literature. Where, D_v is the diffusion coefficient of oxygen vacancies, k_f and k_r are, respectively, the forward and reverse reaction rate constants as discussed below. A complete oxygen permeation model is developed in the present study as it is discussed later in the coming section. The flow rates in SI units (kg/s) have been calculated from feed and permeate side volume flow rates (in sccm) using the species concentrations at inlet and the species properties calculated at the standard conditions of 0 °C. The analyses of the reaction kinetics are done here using a two-step model in order to consider the detailed oxy-combustion process without large computational effort.

TABLE 4.1 Membrane specifications as described in Nemitallah et al. [183].

Parameter	Value
Membrane thickness	0.9 mm
Membrane material	LSCF-1991
density	6000 kg/m ³ [184,185]
Thermal conductivity	4 W/m/K [184,185]

4.1.2 2D analysis Reaction kinetics model

In this part of the work and due to the reduced coordinate system to 2D due to symmetry in the reactor design, the two-step hydrocarbon oxidation mechanism by Westbrook and Dryer [181] which was modified by Andersen et.al. [29] is used for the calculations of the reaction kinetics, since this scheme is directly available as default in the commercial CFD code Fluent. The model was modified to handle the increased CO₂ concentration under oxy-fuel conditions. The Westbrook and Dryer model [181] consists of two reactions, where the last step, oxidation of CO to CO₂, is reversible. The mechanism is listed in the form of three irreversible steps as described above in the part of numerical modeling setup for the gas turbine model combustor (see reactions from 1 to 3 above). For this model, the modified reaction rate data by Andersen et.al. [29] are listed as described in table 3.1.

4.2 3D membrane reactor model setup

Little work was reported with a focus on examining the effects of reaction side conditions and flow configuration on oxygen permeation through the mixed-conducting ceramic membranes and none has been performed for 3-D membrane reactors. In the present study, focus is made on oxygen separation through ion transport membranes and then the combustion is made in the permeate channels with fuel in a mixture of O₂/CO₂/H₂O. The new reactor design introduced here is substituting conventional gas turbine combustor by a monolith structure ITM reactor. Optimization for the feed and sweep flow rates have been done in order to meet the power required for the reactor and keeping the reactor size as compact as possible. Effects of flow configurations, channel width and percentage of

CH₄ in the permeate side flow are also introduced under constant inlet gas temperature and fixed operating pressure of 10 bars. Since reported maximum permeation rates have increased relatively recently [164], the expression in their study was scaled up by one order of magnitude (inside the model) such that it gives the maximum flux values found in the literature at maximum temperature and partial pressure difference and to reflect recent permeation improvements. However, different oxygen permeation model is used in the present study, the same scaling factor like that in [164,186] has been applied to the model in order to reflect the recent improvements in the oxygen permeation. The reactor geometry has been optimized based on the optimization of channel width. Accordingly, the number of permeate and feed channels has been calculated keeping the reactor size as close as possible to the size of a real industrial gas turbine. The monolith structure reactor design introduced here is able to give power ranging from 5 to 8 MWe based on cycle first law efficiency.

4.2.1 3D reactor specifications and operating conditions

A monolith structure design ITM reactor is used here in the present study with total number of feed and permeate channels of 50,000, 25,000 for each stream. Each channel has a square cross section of width of 15 mm based on the channel width optimization as discussed in the coming section. The length of the reactor was considered fixed and equal to 0.9 m in order to keep the length of the reactor to be similar to that of real industrial gas turbines. Due to symmetry in the monolith structure design of the reactor, only 3D four quarters of four adjacent channels sharing one common edge are considered in all simulations as shown in Fig.4.2. The section in Fig.4.2 is for a traverse cross section in

four adjacent channels inside the reactor and normal to the axial 'z' direction. As shown in the figure, LSCF-1991 ionic ceramic membranes separate oxygen containing streams (typically air) from streams containing the fuel, methane, and the sweep gas, CO₂ plus H₂O. More details about membrane specifications are there in table 4.1 as described in our previous work, Nemitallah et al. [183]. The present reactor design results in reactor height of 3.35 m and overall volume and membrane surface area of 10.1 m³ and 2700 m², respectively. In order to understand how an ITM reactor depends on the flow configuration, calculations are performed for co-current versus counter current at the same operating conditions. Restricted equilibrium is assumed for simplicity because it provides upper-bound estimates on the wall temperature and reactive ITM performance in general.

The channel width is varied in this study in order to investigate the effect of reactor geometry on oxygen permeation flux and combustion process. The temperature of streams in all feed and permeate channels of the reactor is fixed to 900 °C and the pressure for all streams is maintained at ten times the atmospheric pressure, 10 bars. Optimizations of the volume flow rates of feed and permeate flows have been done in order to get maximum oxygen permeation flux and improving the combustion process in the permeate channels. The pre-exponential coefficients of the Dkk (D_v , K_f and K_r coefficients model) oxygen flux permeation equation model have been fitted using the available experimental data in literature. Where, D_v is the diffusion coefficient of oxygen vacancies, k_f and k_r are, respectively, the forward and reverse reaction rate constants as discussed below.

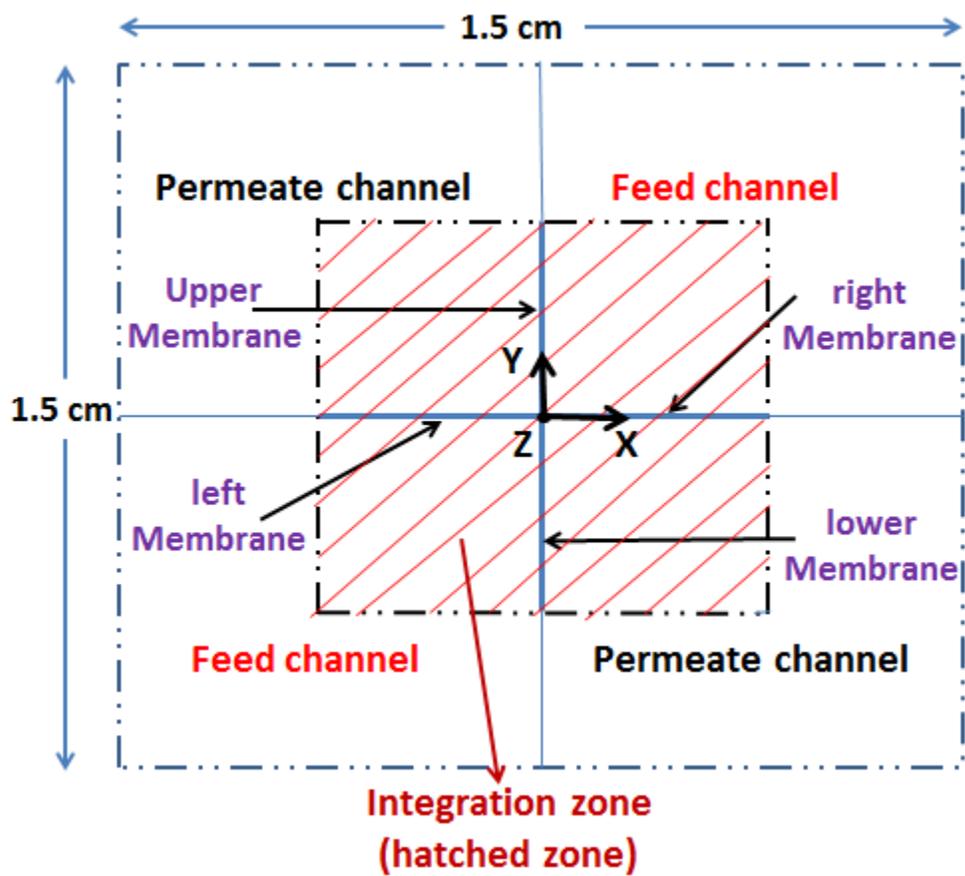


Figure 4.2 Schematic diagram of a traverse cross section in four adjacent channels in the 3-D membrane reactor showing the membranes and the considered integration zone.

4.2.2 3D analysis reaction kinetics model

The simplest oxidation mechanism assumes that products of the chemical reaction consist only of CO₂ and H₂O:



The physical situation that this assumption reasonably approximates is a diffusion flame suspended in the flow field at relatively high temperature [186]. Here, the oxygen diffuses across the boundary layer to meet methane in a small, well-defined reaction zone. The high temperature of the flame accelerates the local homogeneous kinetics, and mostly produces CO₂ and H₂O only, if the flame temperature is not too high. However, for the purposes of our model, we need only to show that the reaction rates are so much fast that chemical equilibrium is always locally attained.

Finally, we are also assuming that the homogeneous gas phase reactions in the relatively cool bulk are so slow that once the products of the reaction have formed and leave the reaction zone back to the free stream, they do not have a sufficient residence time to interact and form species such as H₂ or CO.

4.3 Development of oxygen permeation equation

The same oxygen permeation equation is considered in both 2D and 3D membrane reactors simulations. In the ceramic membrane reactor, oxygen permeates through the ionic or mixed-conducting ceramic membrane via a complex mechanism. It usually includes adsorption of oxygen and charge transfer reaction on the membrane surface

exposed to air, oxygen vacancy and electron diffusion in the membrane bulk, and charge transfer and chemical reaction on the membrane surface exposed to a reducing gas. The detailed mathematical formulation for oxygen permeation through mixed-conducting ceramic membranes is fairly complex [129]. Only mobile ionic defects can move from one lattice position to another, and the oxygen vacancy and electron hole are the two charged defects in ITM. When an oxygen vacancy moves to the site occupied by an oxygen ion, the oxygen ion is relocated to the site released by the oxygen vacancy. The transport of charged defects at steady state under an electrochemical potential gradient is described by the Nernst–Planck equation:

$$J_v = -\frac{\sigma_v}{4F^2}(\nabla\mu_v + 2F\nabla\Phi) \quad (4.2)$$

Where σ_v is the oxygen vacancy conductivity; $\nabla\mu_v$ and $\nabla\Phi$ are the gradients of the chemical potential and the electric field, respectively. Because of the fast transport of electron-holes inside the open-circuit membrane, a steady-state electric field gradient is not established and it can be considered:

$$\nabla\Phi = 0 \quad (4.3)$$

Assuming ideal behavior, the chemical potential gradient can be correlated to the concentration of oxygen vacancies by:

$$\nabla\mu_v = RT\nabla\ln C_v \quad (4.4)$$

Since the thicknesses of the membrane disks are small compared with their diameters, radial diffusion can be neglected. Using Eqs. (4.3) and (4.4) as well as the Einstein

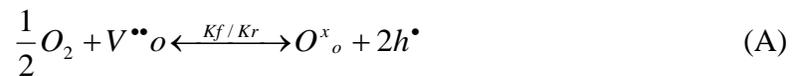
relation ($\sigma_v = (4F^2/RT)C_v D_v$), Eq. (4.2) can be transformed for one-dimensional oxygen permeation to give:

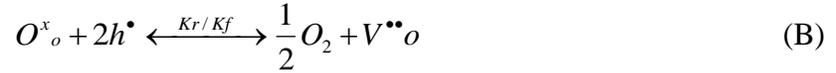
$$J_v = -D_v dC_v/dx \quad (4.5)$$

This takes the form of Fick's first law. According to classical diffusion theories, the diffusion coefficient of oxygen vacancies, D_v , is a function of temperature and the oxygen defect lattice structure. Once the steady-state structure is established under certain temperatures, D_v can be considered constant and not to be a function of the position from the membrane wall. Based on this analysis and considering $J_{O_2} = -\frac{1}{2} J_v$, the oxygen permeation flux (J) via bulk diffusion can be obtained by integrating Eq.(4.5):

$$J_{O_2} = \frac{D_v}{2L} (C''_v - C'_v) \quad (4.6)$$

Where, L is the membrane thickness, C'_v and C''_v are the concentrations of oxygen vacancies at the high and low oxygen pressure sides of the membrane, respectively. This Expression shows that the oxygen permeation rate by bulk diffusion is governed by the ionic conductivity, temperature and the chemical potential gradient of oxygen vacancies across the membrane. The concentration of oxygen vacancies at both surfaces of the membrane (C'_v and C''_v) in Eq. (4.6) is also governed by surface exchange kinetics for the following two surface reactions:





Where. O^x_o represents lattice oxygen in the perovskite crystal structure, k_f and k_r are, respectively, the forward and reverse reaction rate constants for reaction a (or the reverse and forward rate constants for reaction b). It should be noted that because of the high electronic conductivity, the electron holes are essentially constant at both surfaces of the membrane, and thus the reverse reaction rate of Reaction a and the forward reaction rate of Reaction b are pseudo zero-order at steady state under isothermal conditions. While these two reactions may involve many sub-steps, such as oxygen adsorption, dissociation, recombination, and charge transfer, study by van Hassel et al. [187] have theoretically and experimentally demonstrated that these two reactions can be considered as elementary reactions and that the law of mass action is therefore applicable. Therefore:

$$J_{O_2} = K_f P'_{O_2}{}^{0.5} C'_v - K_r \quad (4.7)$$

$$J_{O_2} = K_r - K_f P''_{O_2}{}^{0.5} C''_v \quad (4.8)$$

As proposed by Xu and Thomson [130], at steady state, an expression that combines surface exchange on the feed and permeate sides and bulk diffusion in terms of the oxygen partial pressures can be derived. At steady state, Eqs. From (4.6) to (4.8) are equal. Combining these expressions, we obtain the desired form:

$$J_{O_2} = \frac{D_v K_r (P'_{O_2}{}^{0.5} - P''_{O_2}{}^{0.5})}{2LK_f (P'_{O_2} P''_{O_2})^{0.5} + D_v (P'_{O_2}{}^{0.5} + P''_{O_2}{}^{0.5})} \quad (4.9)$$

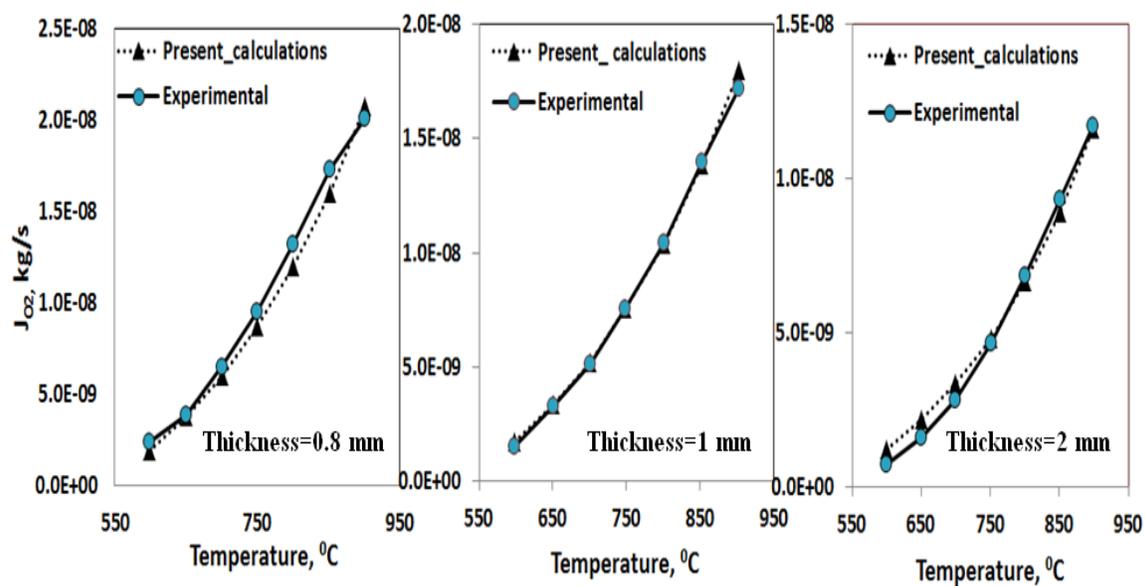


Figure 4.3 Fitting of the experimental data of Kusaba et.al.[163] for Oxygen permeation through LSCF1991 membrane having thicknesses of 0.8, 1 and 2 mm with the present permeation model [183].

Where, D_V , K_r and K_f are functions of temperature and the specific properties of the membrane. D_V is the diffusion coefficient of oxygen vacancies and k_f and k_r are, respectively, the forward and reverse reaction rate constants for reaction A (or the reverse and forward rate constants for reaction B). The concentration of oxygen vacancies at both surfaces of the membrane is governed by surface exchange kinetics.

The value of the pre-exponential coefficient of D_V is in m^2/s , of k_f is in $m/atm^{0.5}.s$ and that of k_r is in $mol/m^2.s$. The activation energy for LSCF-1991 membrane has been determined in our work [183] by fitting the experimental oxygen flux data in the work done by kusaba et.al.[163] as function of temperatures as shown in Fig.4.3. As shown in the figure, both the experimental data and the present Dkk model (pre-exponential coefficients of D_V , K_r and K_f model) are in a very good agreement for all of the three considered thicknesses of the membrane. The fitted values of the pre-exponential coefficients of D_V , K_r and K_f are listed in table 4.2 and also the values of the activation energies are listed there in the table.

TABLE 4.2 Obtained pre-exponential coefficients and activation energies by Nemitallah et al. [183] of D_v , k_f and k_r for LSCF-1991 membrane comes from the fitting of experimental data of Kusaba et.al.[163]

Expression	Pre-Exponential coefficients		Activation Energy (kJ/mol)
	Unit	Value	
$D_v = D_v^0 \exp(-E_D/RT)$	m^2/s	1.58×10^{-5}	73.6
$K_f = k_f^0 \exp(-E_f/RT)$	$m/atm^{0.5} \cdot s$	1.11×10^{10}	226.9
$K_r = k_r^0 \exp(-E_r/RT)$	$mol/m^2 \cdot s$	3.85×10^{11}	241.3

4.4 CFD model

The same CFD model is considered in both 2D and 3D membrane reactors simulations. Following the same approach of the previous work [169], the species transport across the membrane is carried out using a source/sink term. The source/sink term (S_i) accounts for the mass flow of species across the membrane. At the volume cells adjacent to the membrane surface, the species are allowed to disappear from one side of the membrane through the sink term and to come out on the other side through the source term. With this method, the velocity and the pressure fields of the gas mixture are obtained from the numerical solution of the mass and momentum conservation equations, while the species concentration distribution and the relevant permeate and retentate fluxes are obtained from a scalar convection-diffusion equation including a source term to tackle the mass flow of the species across the membrane.

The equations which govern the conservation of mass, momentum and energy as well as the equations for species transport are found there in the work done by Lei and Ghoniem [175]. Due to the transfer of oxygen molecules across the membrane surface from feed side to permeate side, a source-sink term should be added to those equations to account for oxygen transfer across the membrane. The conservation equations are modified in our previous works [169,170,183] as follows:

$$\nabla \cdot (\rho U) = S_i \quad (4.10)$$

$$\nabla \cdot (\rho U U) = -\nabla P + \mu \nabla^2 U \quad (4.11)$$

$$(\rho C_p)U \cdot \nabla T = \nabla \cdot (\lambda \nabla T) \quad (4.12)$$

$$\nabla \cdot (\rho U Y_i) - \nabla \cdot (\rho D_{i,m} \nabla Y_i) = S_i \quad (4.13)$$

Where, u is the velocity vector, ρ is the fluid density, p is the pressure, μ is the dynamic viscosity, λ is the thermal conductivity, $D_{i,m}$ is the diffusion coefficient, Y_i is the scalar species mass fraction and S is a source/sink term. In all cases, the source/sink term, S , permits taking into account the mass flow of the species across the membrane. Clearly, the method requires the preliminary knowledge of the permeability characteristics of the membrane, which determine the formulation of the source term. In this work, LSCF1991 membrane have been considered, which is permeable to oxygen only. Therefore, the source term only takes into account the transfer of oxygen molecules across the membrane. Depending on each specific membrane, any mechanism can be included in the model. From the above mentioned oxygen permeation equation (Eq.4.9), the following form for the source term can be implemented in the model:

$$S_i = \begin{cases} + \frac{J_{O_2} \cdot A_{cell} \cdot MW_{O_2}}{V_{cell}} & \text{at low partial pressure } O_2 \\ - \frac{J_{O_2} \cdot A_{cell} \cdot MW_{O_2}}{V_{cell}} & \text{at high partial pressure } O_2 \end{cases} \quad (4.14)$$

Where, A_C and V_C is the computational cell area (m^2) and volume (m^3), respectively. MW_{O_2} is the molecular weight of O_2 in kg/mole and J_{O_2} is the oxygen permeation flux in mole/ m^2 -s. The source/sink S_i term (kg/ m^3 /s) is modeled in such a way that it is zero unless $i=O_2$ and the computational cell is adjacent to the membrane surface. Coupling of heat transfer through the membrane surface between feed and permeate sides is made

through a heat balance equation which considers also the radiant heat absorbed by the membrane:

$$Q^{\circ}_{\text{sweep}} - Q^{\circ}_{\text{feed}} - 2\sigma\epsilon(T_{\text{mem}}^4 - T_{\infty}^4) = 0 \quad (4.15)$$

Where, Q°_{sweep} is the heat transfer from the reacting sweep gases to the membrane and Q°_{feed} is the heat released from the membrane surface to the feed side. The emissivity of the membrane surface is assumed to be equal to 0.8 and T_{mem} and T_{∞} are the membrane and surrounding wall temperature, respectively. The diffusion coefficient is determined by specifying, the binary mass diffusion coefficient of the component i in the component j . The corresponding diffusion coefficient is:

$$D_{i,m} = \frac{1 - X_i}{\sum_{j,i \neq j} \left(\frac{X_j}{D_{i,j}} \right)} \quad (4.16)$$

Gambit 2.2 was used to construct the 2D and 3D meshes. For the 2D reactor simulations, only half part of the reactor was modeled due to reactor symmetry with a mesh of more than 5,00,000 finite volumes was used with very small boundary control volumes near to both sides of the membrane in order to correctly predict the permeation process. For the 3D membrane reactor simulations, a mesh has been constructed with more than 1,000,000 finite volumes was used with very small boundary control volumes near to both sides of the membranes. The general-purpose commercial CFD code Fluent 12.1 was selected for the solution of the steady-state conservation equations adopting the laminar formulation for all simulations. Grid independence has been performed to get unchangeable accurate calculations. The equations were numerically solved in a Cartesian coordinate system; Transport of O_2 across the membrane was achieved using series of user-defined functions (UDF) that are written in VC++ and compiled and

hooked to the FLUENT software. The issue of hydraulic jump across the membrane was resolved by patching the cells from the upper and lower zones with two different values of initial partial pressures of species. The convective terms were discretized by a second order upwind scheme, while the SIMPLE algorithm was used in all cases to couple the continuity and Navier -Stokes equations, due to its stability and accurateness. The solution convergence was carefully checked by monitoring the residuals of all variables as well as the species mass flow rate. Residuals were dropped to the order of 10^{-5} or less, which is at least 2 orders of magnitude tighter than Fluent's default criteria.

4.5 Radiation heat transfer modeling

Same radiation model has been applied for all 2D and 3D simulations. In order to correctly predict the temperature distribution in the membrane reactor, a radiative transfer equation (RTE) for an absorbing, emitting and scattering medium has to be solved. The RTE equation is written as:

$$\frac{dI(\mathbf{r}, \mathbf{s})}{ds} = \kappa I_b - (\kappa + \sigma_s)I(r, s) \quad (4.17)$$

The total radiation intensity I , depends on the position vector, r , and the path length s . κ is the absorption coefficient and σ_s is the scattering coefficient. The Planck mean absorption coefficient is given as:

$$\kappa_p(T, P) = \frac{\int_0^\infty \kappa_\lambda(\lambda, T, P) e_{b\lambda}(\lambda, T) d\lambda}{\sigma T^4} \quad (4.18)$$

Where, $e_{b\lambda}$ is the blackbody spectral emissive power. κ is calculated using variables by Liu et al. [188].

An accurate calculation of the gas radiation property must consider the spectral absorption of CO_2 and H_2O , and also the overlap between these radiating gas components. Since direct prediction of the absorption coefficient is computationally complex, models for absorption properties, such as the gray gas, will have to be employed in the radiation heat transfer model. The most commonly used gray gas model in CFD is the weighted sum of gray gases (WSGG) model proposed by Smith et al. [189] has been applied in the present CFD calculations. In this model, the gas is assumed to consist of a transparent gas and several gray gases without any wavelength dependence, and the model parameters are based on the radiation properties of air-fired flue gases.

CHAPTER 5

RESULTS AND DISCUSSIONS FOR THE GAS TURBINE

MODEL COMBUSTOR

In this part of the present research work, experimental and numerical investigations of an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor are presented. Oxy-combustion and emission characterization, flame stabilization and oxy-combustion model validation analyses are the main goals of the present work. The combustor is fuelled with CH_4 and a mixture of CO_2 and O_2 as oxidizer. Wide ranges of different operating parameters are considered including equivalence ratio, percentage of O_2/CO_2 in the oxidizer mixture, and fuel volume flow rate. The study aims to check the stability of the oxy-combustion diffusion flame experimentally and numerically and also to check the minimum permissible percent of O_2 in the oxidizer mixture required in order to get a stable flame. Visualizations of the flame at the above mentioned operating conditions have been carried out experimentally and comparisons with the numerical results have been done. The flames have been characterized in details by measuring the exhaust gas temperatures and comparing them with those from the numerical model. Flame zone also has been characterized in details by plotting the axial and radial

temperatures, species concentrations and flow velocities. A modified two-step oxy-combustion reaction kinetics model for methane-oxygen combustion has been used in order to predict a clearer oxy-combustion characteristics and then more accurate numerical results in order to correctly validate the numerical model using the experimental results.

5.1 Flame stabilization behavior

A series of experiments in a swirl-stabilized gas turbine model combustor described above has been carried out at atmospheric pressure for a range of parameters including fuel volume flow rate, percentage of O₂ in the oxidizer mixture and equivalence ratios. The stability of the oxyfuel/CH₄ flames was studied for Oxygen concentrations in the oxidizer mixture starting from 100 % and reducing this percent till the flame blow out state. The equivalence ratio has been changed from 0.5 to 1 and fuel volume flow rate from 5 L/min to 10 L/min. However, attempts of operating the burner with less than 21% O₂ were unsuccessful in all of the considered operating range resulting in unstable operation and blow out. Table 5.1 presents the values of the percentages of O₂ in the oxidizer mixture (remainder is CO₂) at which the flame has reached a blow out condition. It seems from those results that the most stable flame for the present design is at equivalence ratio of 0.65, as the flame blows out at minimum possible percentage of O₂ for stable flame, 22 % at 6 L/min fuel volume flow rate and 21 % at 9 L/min fuel volume flow rate. As the equivalence ratio was increased more than 0.65, the flame instability conditions are encountered and the flame blow out occurred at higher percentage of O₂ in the oxidizer mixture. This is due to the reduced amount of oxygen available for

combustion in the flame zone. As the equivalence ratio is increased as in the present model of gas turbine combustor, a great portion of the inlet oxidizer is escaping near to the combustor wall around the flame in order to cool down the exhaust gases comes out from the combustion process. When the equivalence ratio was decreased lower than 0.65 also another cause for instability was encountered because of the increased amount of CO₂ available in the combustion chamber which reduces the burning velocity and results in poor combustion performance and a modified distribution of temperature and species in the combustion chamber. The lower burning velocity for oxy-combustion of gaseous fuel theoretically can be affected by the following features: (1) lower thermal diffusivity of CO₂, (2) higher molar heat capacity of CO₂, (3) chemical effects of CO₂ and (4) modified radiative heat transfer [18]. Since the molar heat capacity affects the flame temperature, its effect generally dominates.

TABLE 5.1 The percentage of O₂ in the oxidizer mixture at which the flame blows out at different equivalence ratios and fuel volume flow rates.

Equivalence ratio, ϕ	$V_f^0 = 6$ L/min	$V_f^0 = 9$ L/min
0.5	24	22
0.55	23	22
0.65	22	21
0.75	25	25
1.0	25	25

To visualize the flame shape, a high speed camera has been used to record the flame photos under steady state operating conditions. The displayed images cover a field of view of the whole reactor height (300 mm). Figure 5.1 shows a Comparison between experimental (photo using a high speed camera) and numerical (taken from temperature contour plots) flame shapes at different equivalence ratios, $V_f=6$ L/min and $O_2/CO_2:50/50\%$. As it is clear from the figure, the calculated flame shape using the contour plots of temperature distribution is very close to the experimental recorded shapes taken from the steady state flame photos. This is a very good agreement however; the experimental photos are not showing the regions of small temperature gradients. At the lower equivalence ratios, the combustion is stable due to excess oxygen available in the combustion region and the flame temperature as a result increase as characterized from the flame shape and color as shown in the figure.

As the equivalence ratio increases, the red part of the flame increases indicating less oxygen availability in the flame zone. That's why the flame starts to extend for more distance inside the reactor in order to complete the combustion process. As a result, the temperature of the flame was reduced as will be discussed in the next section. At higher equivalence ratios, the combustor enters an unstable mode; completely unstable combustion was encountered in case of equivalence ratio equal to 1.0 as shown in the figure. The video images show clear signs of an axially symmetric vortex ring structure forming at the sudden expansion and moving through the outer recirculation zone near to reactor wall.

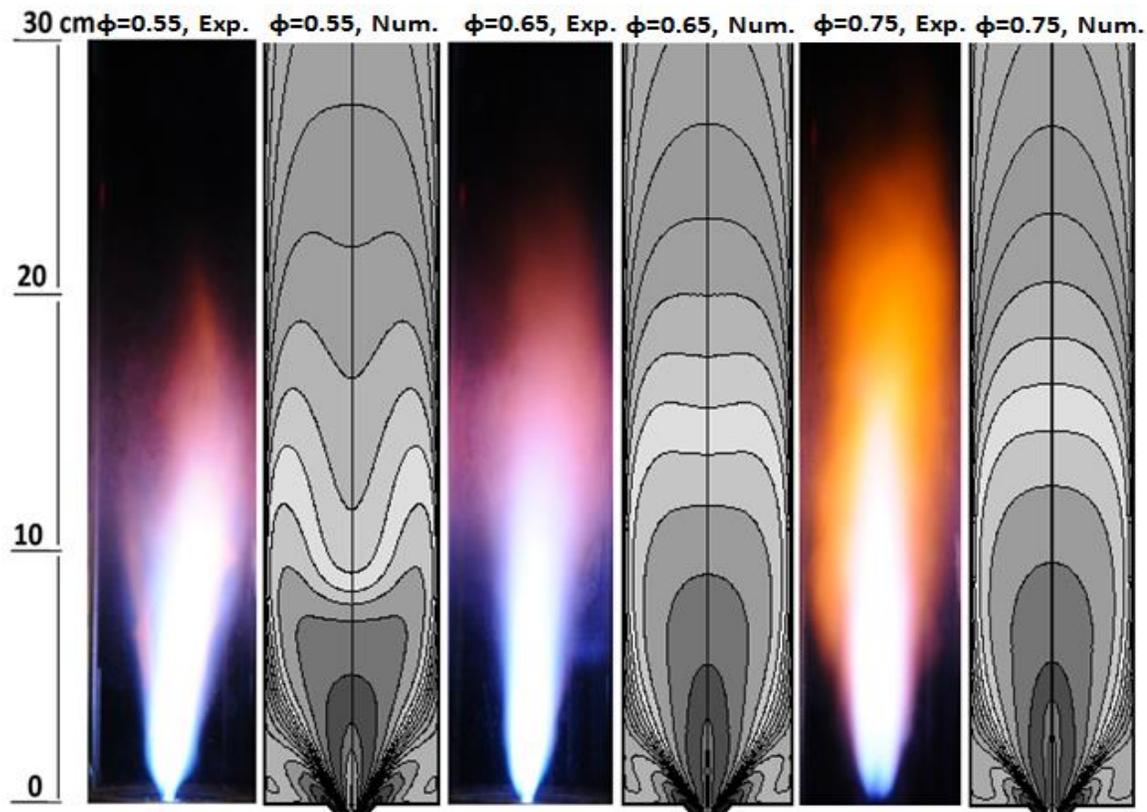


Figure 5.1 Comparison between experimental (photo using a high speed camera) and numerical (taken from temperature contour plots) flame shape at different equivalence ratios, $V_f=6$ L/min and $O_2/CO_2:50/50\%$.

Figure 5.2 shows the percentages of O_2 in the oxidizer mixture at constant fuel volume flow rate of 6 L/min considering two operating equivalence ratios. The images indicate that as the O_2 content in the oxidizer is increased the flame can be operated stably. This can be attributed to two effects: the flame speed and/or the Reynolds number. As shown in the figure for both equivalence ratios, the flame is stable for higher concentrations of O_2 and as the percentage of CO_2 increases in the mixture as the flow rate increases (constant equivalence ratio) and the start to be lifted at 40%/60% of O_2/CO_2 . As the percentage of O_2 in the oxidizer mixture is reduced more, the flame lift distance increases and occupies smaller area inside the reactor until the blow out point is encountered between 25 to 22 % of O_2 in the oxidizer mixture. In oxyfuel combustion the O_2 fraction of the oxidizer can be seen as an additional variable influencing the combustion behavior.

In fact, the O_2 concentration has a large effect on increasing the flame speed. The oxidizer composition also influences the flow field as the Reynolds number increases as the percentage of CO_2 increases in the oxidizer mixture due to its higher molecular weight. The higher flame speed and lower Reynolds number hence assist flame stabilization and lean operation at higher O_2 levels. Also, the flames at higher oxidizer flow rates (lower equivalence ratio and higher Reynolds number) have similar stability limits.

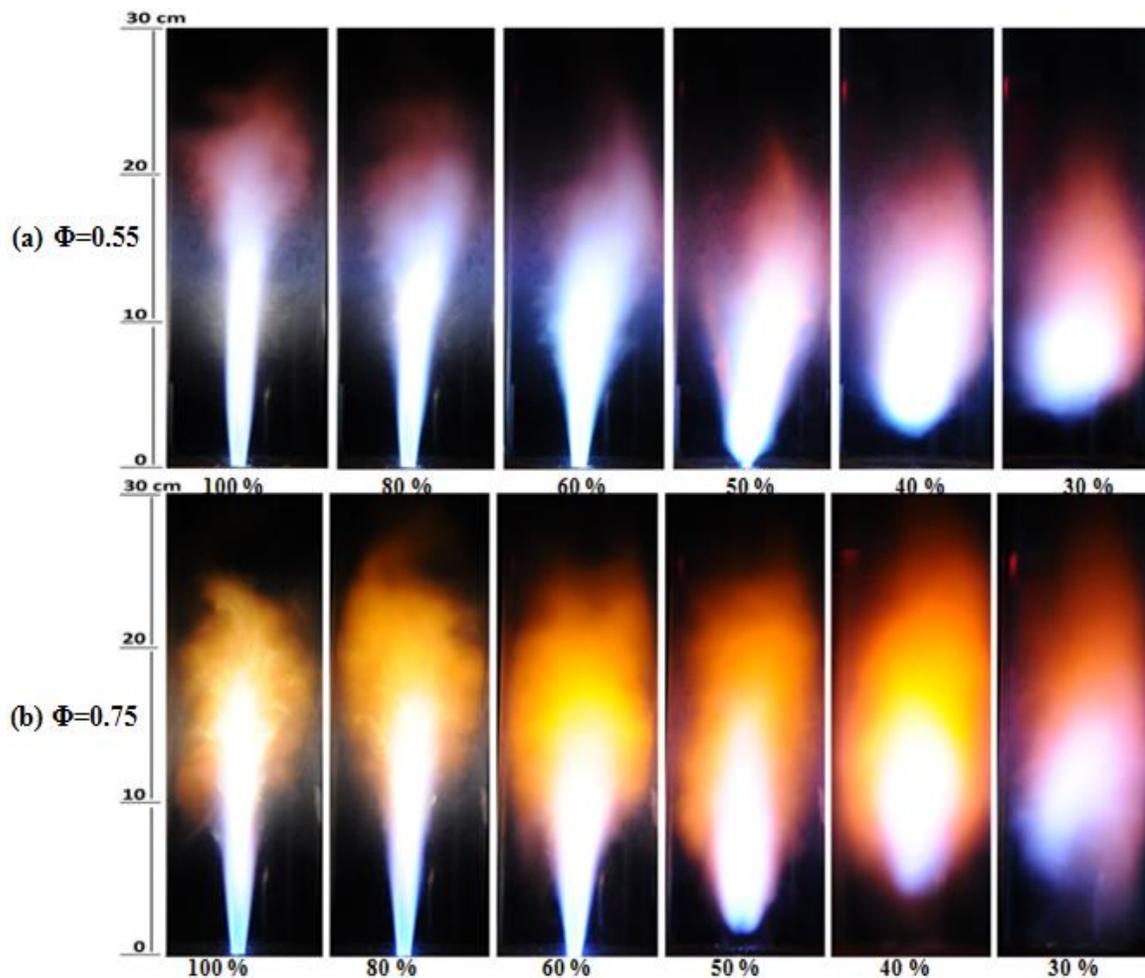


Figure 5.2 Visualization of the flame shape using images captured at steady state operation to investigate the effect of concentration ratio of O_2 in the oxidizer mixture at fixed fuel volume flow rate of 6 L/min: (a) at $\phi=0.55$ and (b) at $\phi=0.75$.

The stabilization behavior does not change significantly with changing the fuel volume flow rate as can be seen in Fig.5.3 by comparing the images for the same equivalence ratio for the two considered fuel volume flow rates, 6 L/min and 9 L/min. all the images recorded in the figure are at 60%/40% of O₂/CO₂ in the oxidizer mixture to correctly analyze the effect of equivalence ratio on the flame stabilization. In each case for a given fuel volume flow rate, we have observed a similar series of transitions in the combustor dynamics and flow noise as characterized by the flame shape as shown in the Fig.5.4. However, in case of 9 L/min fuel flow, the flame was lifted for all equivalence ratios causing more noise of the flame.

At the lower equivalence ratios, the combustion is stable due to excess oxygen available in the combustion region and the flame temperature as a result increase as characterized from the flame shape and color as shown in the figure. As the equivalence ratio increases as the red part of the flame increases indicating less oxygen availability in the flame zone and that's why the flame starts to extend for more distance inside the reactor in order to complete the combustion process and as a result, the temperature of the flame was reduced as will be discussed in the next section.

At higher equivalence ratios, the combustor enters an unstable mode; completely unstable combustion was encountered in case of equivalence ratio equal to 1.0 as shown in the figure. The video images show clear signs of an axially symmetric vortex ring structure forming at the sudden expansion and moving through the outer recirculation zone near to reactor wall.

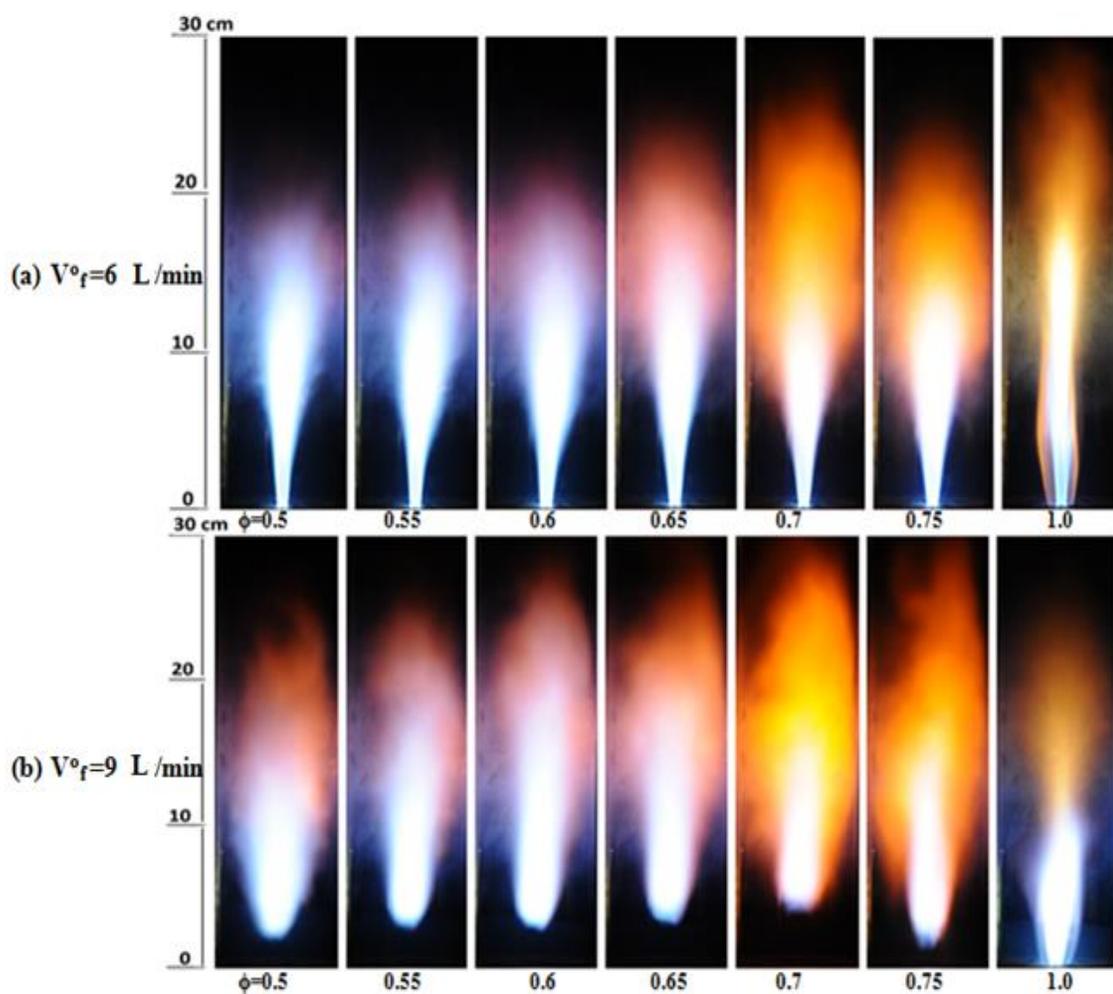


Figure 5.3 Visualization of the flame shape using images captured at steady state operation to investigate the effect of equivalence ratio on flame shape and stability at fixed ratio of O_2/CO_2 , 60%/40% in the oxidizer mixture: (a) at $V_f^0 = 6$ L/min and (b) at $V_f^0 = 9$ L/min.

5.2 Exhaust gas temperature

For CH₄/oxy-combustion, the flames were subject to thermo-acoustic instabilities over a substantial range of operating conditions. As shown in Fig.5.4, at equivalence ratio of 0.55, part (a), the exhaust gas temperature increases at the same radial position with increasing O₂ content in the oxidizer mixture. This is attributed to the higher flame temperature which causes an increase in the reactivity leading to higher laminar flame speeds and shorter ignition delay times. The temperature is maximum at the centerline and decrease toward the reactor wall. The change in chemical reaction rates along with the reduced Reynolds numbers are expected to be main causes for the change of the flame structure when changing the percentage of oxygen in the oxidizer mixture. In case of lower fuel flow rates, as shown in Fig.5.4, part (a), the flame length decreases as the percentage of CO₂ in the oxidizer mixture increases. Even when the flame is lifted, the flame height is also reduced and as a result, the radial exhaust temperature is reduced. However, in case of higher flow rates as shown in Fig.5.4, part (b), the exhaust temperature is reduced with reducing the Oxygen percent in the oxidizer mixture till 60% and after that the flame starts to be lifted due to increased mass flow rate of the oxidizer mixture causing an increase in the exhaust gases temperature at the exit section of the reactor. Further reduction in the percentage of O₂ in the mixture (increasing CO₂) leads to a significant influence on the combustion intensity and stability. As a result, the exhaust gases temperature starts to be reduced again.

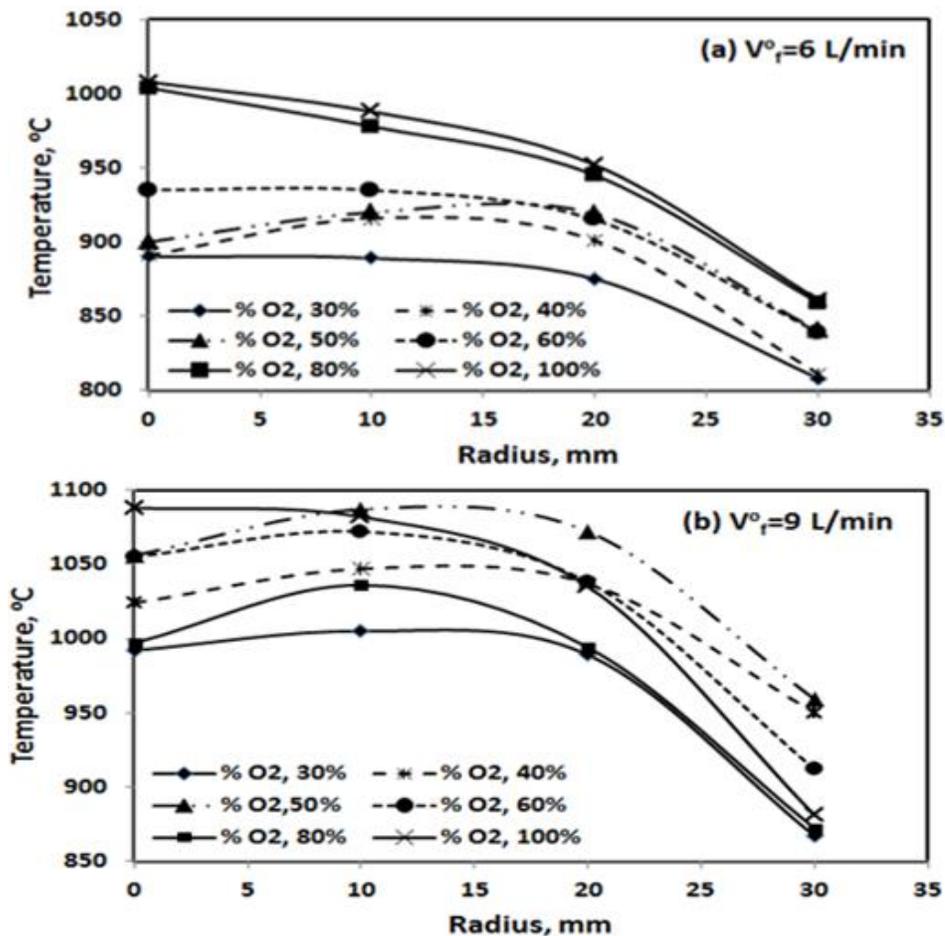


Figure 5.4 The exhaust gases temperature (at a height of 300 mm from the reactor base) radial profiles plots as function of percentage of O₂ in the oxidizer mixture at equivalence ratio of 0.55: (a) at 6 l/min fuel flow rate and (b) at 9 l/min fuel flow rate.

At higher values of equivalence ratios, the flame length is extended as compared to lower values of equivalence ratio. This is due to the reduced oxygen in the flame zone and as a result, the exhaust temperature is increased at lower values of fuel volume flow rates. At higher fuel volume flow rates, the trend is not affected significantly by changing the equivalence ratio. The temperature decreases first with reducing O_2 in the oxidizer mixture then, it increases due to the flame lift. As the amount of CO_2 increases in the mixture, the flame temperature starts to be reduced again. To investigate more clearly the effect of equivalence ratio on the combustion temperature and then on the exhaust gases temperature, Fig.5.5 is showing this effect at two different fuel volume flow rates of 6 and 9 L/min.

At lower fuel flow, part (a), the amount of corresponding oxidizer is low and as the equivalence ratio increases, the availability of Oxygen is reduced causing lower values of the exhaust gas temperature. However, at higher values of fuel flow rates, part (b), the amount of corresponding oxidizer at the same equivalence ratio is increased. As a result the exhaust gas temperature is increased first due to the optimum availability of oxygen inside the flame zone at equivalence ratio of 0.65. Further increase in the equivalence ratio leads to reduced oxygen availability and the exhaust temperature is reduced as shown in Fig.5.5. Note that, in this design of gas turbine, great portion of incoming fresh gases go beside the flame in order to cool down the exhaust gases and that's why the temperature is reduced by increasing the equivalence ratio toward stoichiometry.

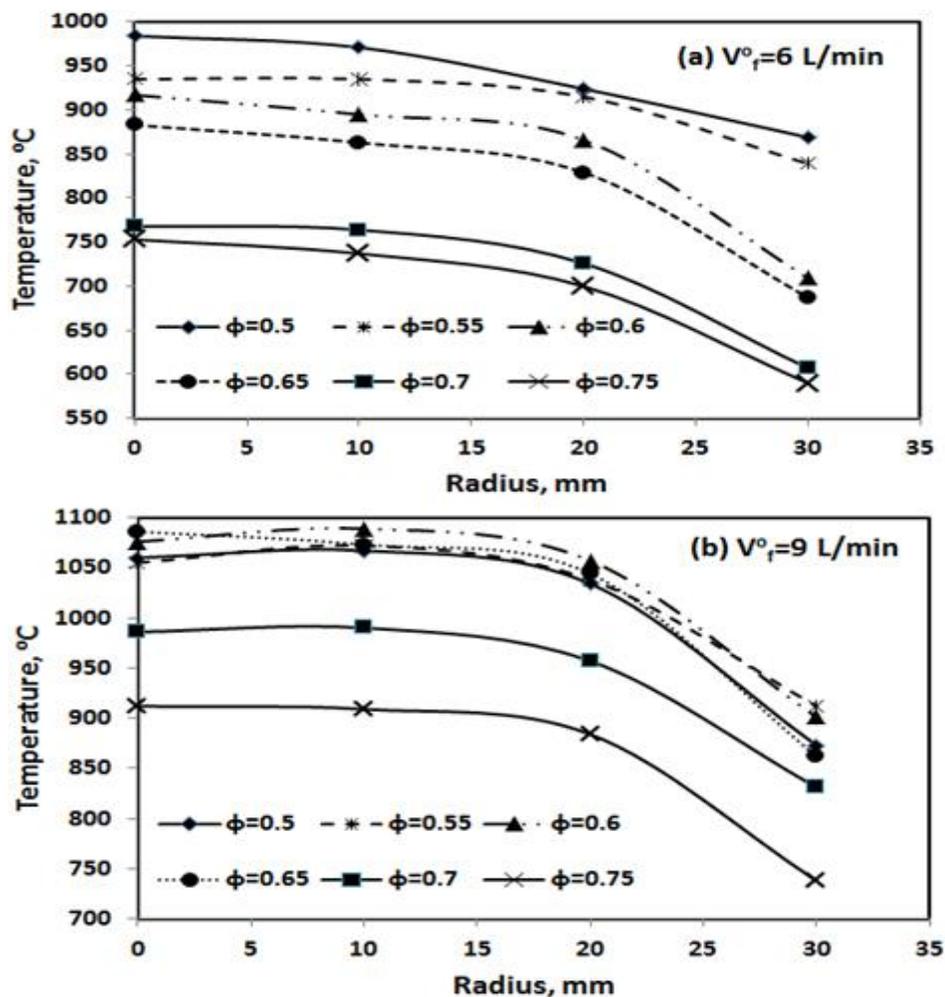


Figure 5.5 The exhaust gases temperature (at a height of 300 mm from the reactor base) radial profiles plots as function of equivalence ratio at 60% O₂ in the oxidizer mixture (40% CO₂): (a) at 6 l/min fuel flow rate and (b) at 9 l/min fuel flow rate.

The average temperature at the exhaust section has been calculated based on energy calculations from flow characteristic data at the exhaust section of the reactor. Those flow data are flow velocity calculated using the 7th power law (for turbulent flow), flow density and flow specific heat at constant pressure calculated at each point and then averaged for the exhaust gases mixture. Based on this energy averaging, the average exhaust gases temperature at a height of 300 mm has been calculated and plotted as shown in Fig.5.6.

Figure 5.6 shows the average exhaust gas temperature as a function of percentage of oxygen in the oxidizer mixture in the upper plot and also as a function of equivalence ratio in the lower plot. At fuel volume flow rate of 6 L/min, the exhaust gas temperature increases with increasing the percentage of oxygen in the oxidizer mixture and decreases with increasing the equivalence ratio as shown in the figure. For the case of 9 L/min fuel flow rate, the temperature is reduced by reducing Oxygen in the mixture until the flame lift occur at about 60 percent O₂ in the oxidizer mixture and then the exhaust temperature will start to be increased. Further increase in the amount of CO₂ leads to the appearance of bad effects of CO₂ on the flame characteristics and as a result, the exhaust temperature is reduced again. Also, the temperature is reduced with increasing the equivalence ratio for the case of 9 L/min fuel flow rate. The analysis of the average exhaust gas temperature is similar to what we have mentioned above however, the average temperature given here is giving an indication about the average energy contained in the exhaust gases.

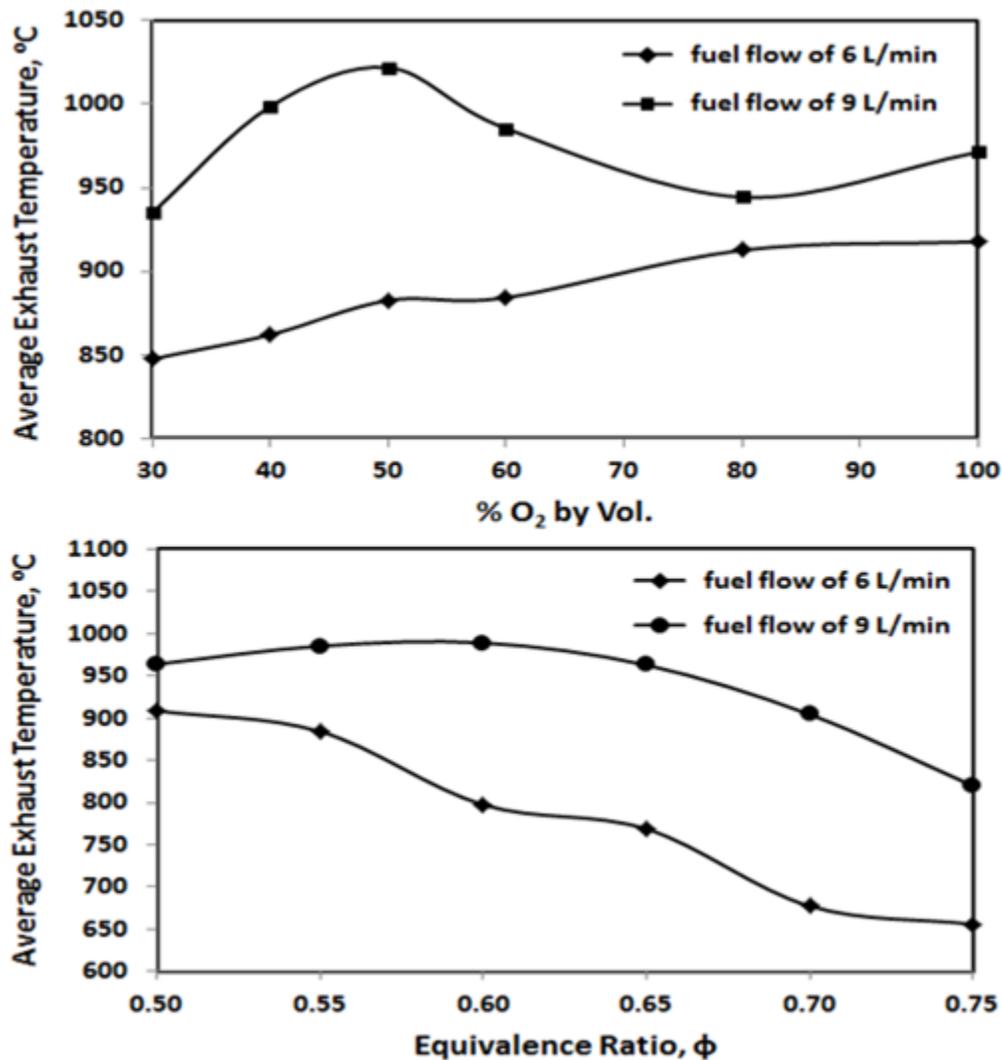


Figure 5.6 Average exhaust gases temperature (at a height of 300 mm from the reactor base) plot at different fuel volume flow rates. (a) as a function of percentage of O₂ in the oxidizer mixture at equivalence ratio of 0.55 and (b) as a function of equivalence ratio for 60% O₂ in the oxidizer mixture (40% CO₂).

5.3 Velocity field

The presently developed computational procedure was used to predict the characteristics of the flow field which are presented in the following subsections. Comparisons between experimental and numerical results are also presented. Figure 5.7 shows the axial velocity distribution at different operating conditions including percentages of O_2/CO_2 in the oxidizer at $\Phi=0.65$ and $V_f =6$ L/min, equivalence ratios at $V_f =6$ L/min and $O_2/CO_2:50/50\%$ and fuel volume flow rates at $\Phi=0.65$ and $O_2/CO_2:50/50\%$. From Fig.5.7, it can be seen that there is an internal recirculation zone along the centerline downstream of the burner outlet. This zone is clearly indicated by the negative values of the axial velocity at heights ranging between $h=75$ mm and $h=120$ mm which indicates a reverse flow along and in the vicinity of the burner axis.

The axial velocity peak ranges from 20 to 35 m/s, depending on the operating conditions, at around $h=30$ mm in the axial direction. The swirling oxidizer stream along with the bluff body in the fuel flow pipe creates a region of a severe pressure gradient along the axis and this is responsible for establishing the internal recirculation zone. In the shear layer between the inflow and both the inner and outer recirculation zones, large velocity fluctuations and the low mean velocity generally cause a very high turbulence intensity. Therefore, intense mixing of the cold fresh gas with hot burned gases can be expected in these regions. For percentages of O_2/CO_2 in the oxidizer mixture between 30/70 and 60/40, no much great differences between the axial velocity distributions as shown in Fig.5.7, part (a).

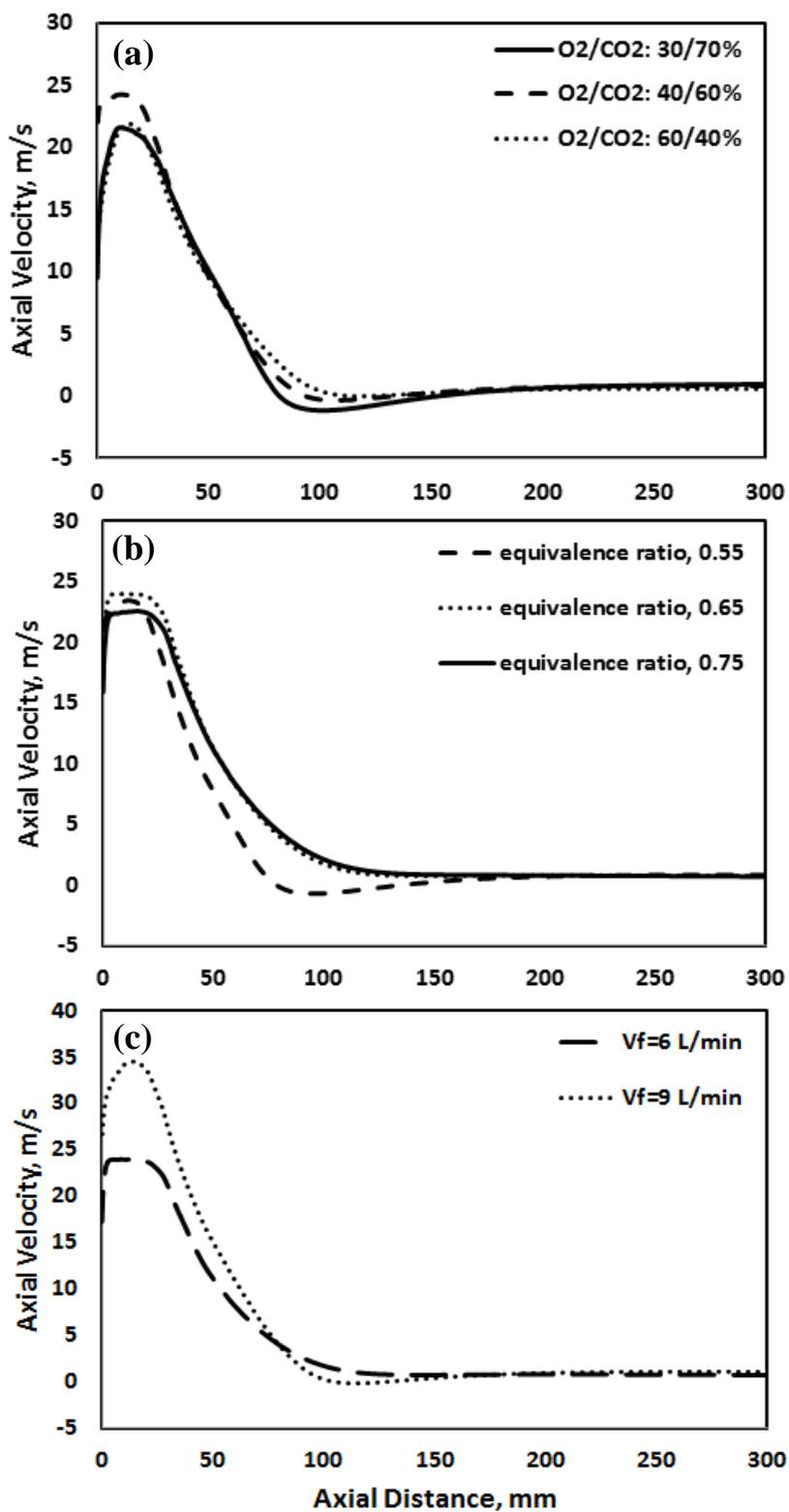


Figure 5.7 Predicted axial velocity distribution at different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and $O_2/CO_2:50/50\%$ and (c) $\Phi=0.65$ and $O_2/CO_2:50/50\%$.

At lower values of equivalence ratios, the recirculation is enhanced in the inner recirculation zone due to the increased amount of oxidizer introduced to the reactor with a swirl angle of 60° as shown in Fig.5.7, part (b). This enhancement in flow recirculation can be seen easily from Fig.5.8 from the distribution of both axial and tangential components of the flow velocity. Also, as the amount of fuel flow increases at fixed operating equivalence ratio, the axial velocity increases and also the recirculation is enhanced as shown in Fig.5.7, part (c). An external recirculation zone near to the reactor wall is also noticed from the contour plots of the tangential velocity as shown in Fig.5.8 and this outer flow recirculation is enhanced by lowering the operating equivalence ratio.

5.4 Temperature and species mole fractions distributions

The distributions of the static temperatures are displayed in Fig.5.9 a and b at the x-symmetry plane of the reactor at $V_f=6$ L/min and $O_2/CO_2:50/50\%$ for two different equivalence ratios. It is seen that the final temperatures of the flames close to exit section of the combustor are increasing with the global equivalence ratios, as expected. This is due to the reduced oxygen availability for combustion at higher values of equivalence ratios and as a result, the flame length is increased. The temperature is maximum in the flame zone close to the reactor center line and it is reduced in the radial direction due to fresh gases inlet. The higher temperatures in the region close to the reactor center line are explained by the more frequent occurrence of reactions. To identify the differences more clearly, Fig.5.10 displays the radial temperature profiles at different heights, $h=25$ mm, $h=50$ mm and $h=100$ mm, at $\Phi=0.65$, $V_f=6$ L/min and $O_2/CO_2:50/50\%$. The high-

temperature region is close to the center line at all heights however; the maximum temperature is reached around $h=50\text{mm}$.

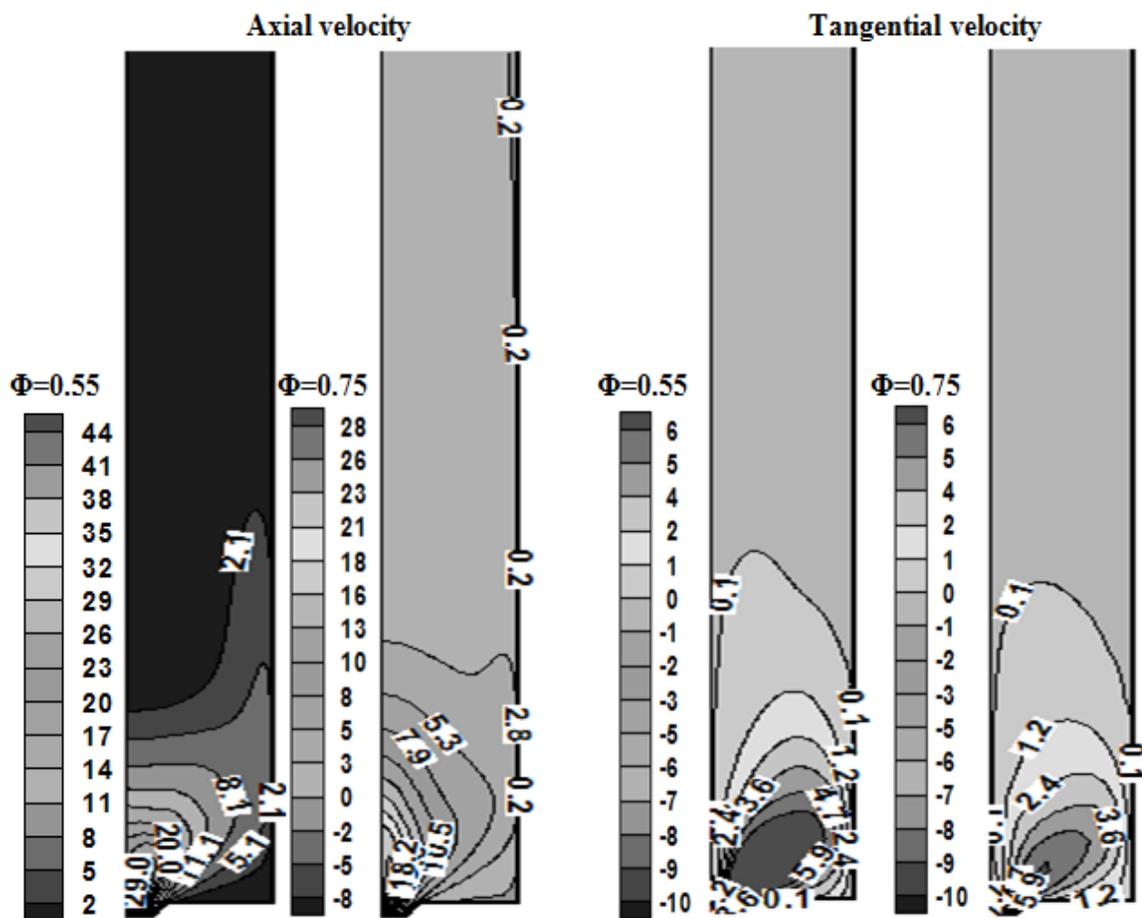


Figure 5.8 Predicted contour plots of axial and tangential velocities at the x-symmetry plane of the reactor at $V_f=6\text{ L/min}$ and $\text{O}_2/\text{CO}_2:50/50\%$ for two different equivalence ratios, 0.55 and 0.75.

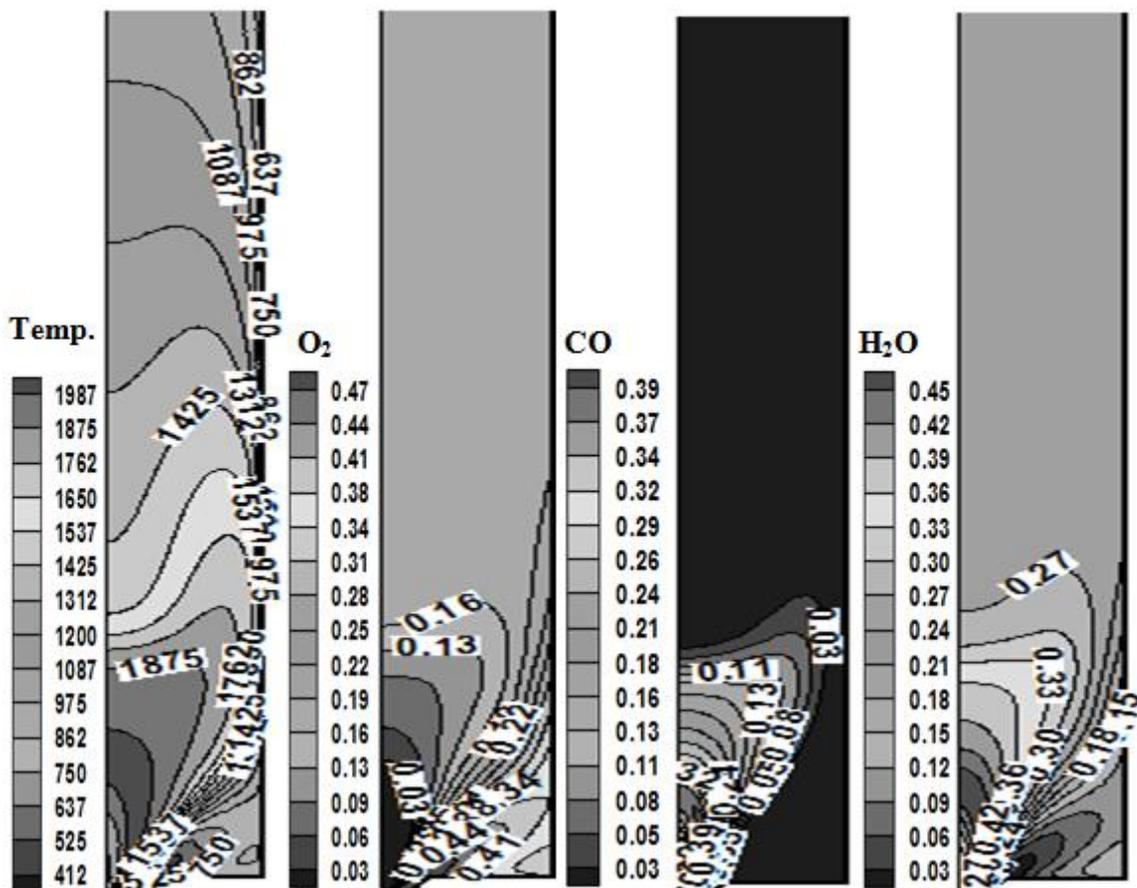


Figure 5.9-a Predicted contour plots of temperature and mole fraction of O₂, CO and H₂O at the x-symmetry plane of the reactor at $\Phi=0.55$, $V_f=6$ L/min and O₂/CO₂:50/50%.

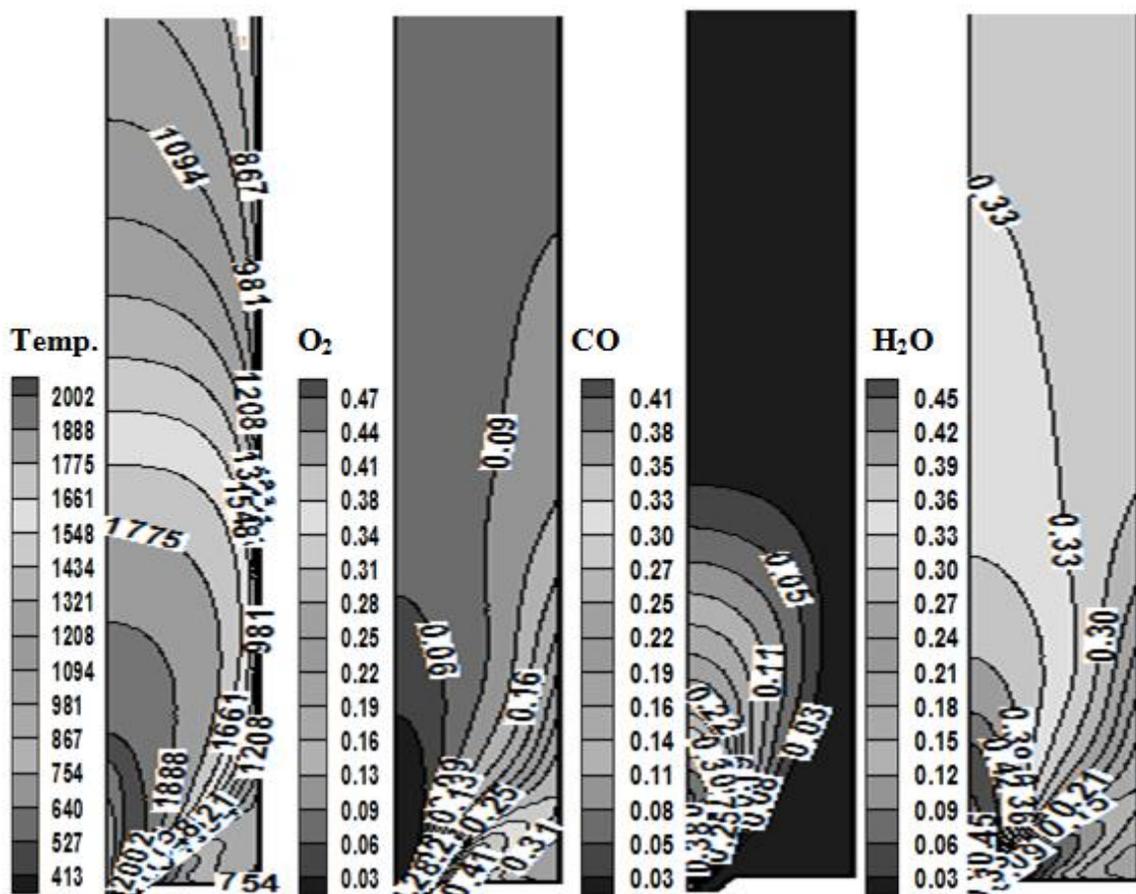


Figure 5.9-b Predicted contour plots of temperature and mole fraction of O₂, CO and H₂O at the x-symmetry plane of the reactor at $\Phi=0.75$, $V_f=6$ L/min and O₂/CO₂:50/50%.

The increased temperature level at $h = 50$ mm enhances, of course, the reactivity of the gas mixtures and, thus, the heat release and burnout as discussed in the coming section. The temperature is reduced in the region at $r \approx 0-5$ mm due to the recirculation in the inner recirculation zone and the reduced temperature at $r \approx 10-20$ mm reflects the inlet streams of fresh oxidizer gas. The temperature level in the outer recirculation zone close to reactor wall is much lower than in the inner recirculation zone, which is due to the leaner mixtures and heat loss through the wall by convection and radiation mechanisms. As the height is increased more than 50 mm, the temperature is also reduced due to the mixing of hot burned gases with the excess unburned oxidizer.

To identify the differences more clearly, Fig.5.11-part (a) displays the axial temperature profiles at different operating percentages of O_2/CO_2 in the oxidizer for $\Phi=0.65$ and $V_f=6$ L/min. With increasing height, temperature values increase strongly, reach a maximum at around $h=50$ mm, and decrease slowly afterward. It has been well established experimentally and numerically that with increasing the percentage of O_2 in the oxidizer mixture, a significantly higher peak as well as overall combustion temperature levels has been encountered (see Fig.5.11-part(a)). The lower combustion temperature in the cases of lower oxygen concentration in the oxidizer mixture is mainly a result of high specific heat capacity of CO_2 . This causes an increase in radiation losses caused by the CO_2 which increases the gas emissivity. The significance of the latter effect obviously depends on the radiative properties of the flame considered, i.e. to what extent other components such as moisture soot and particles contribute to the radiative heat transfer.

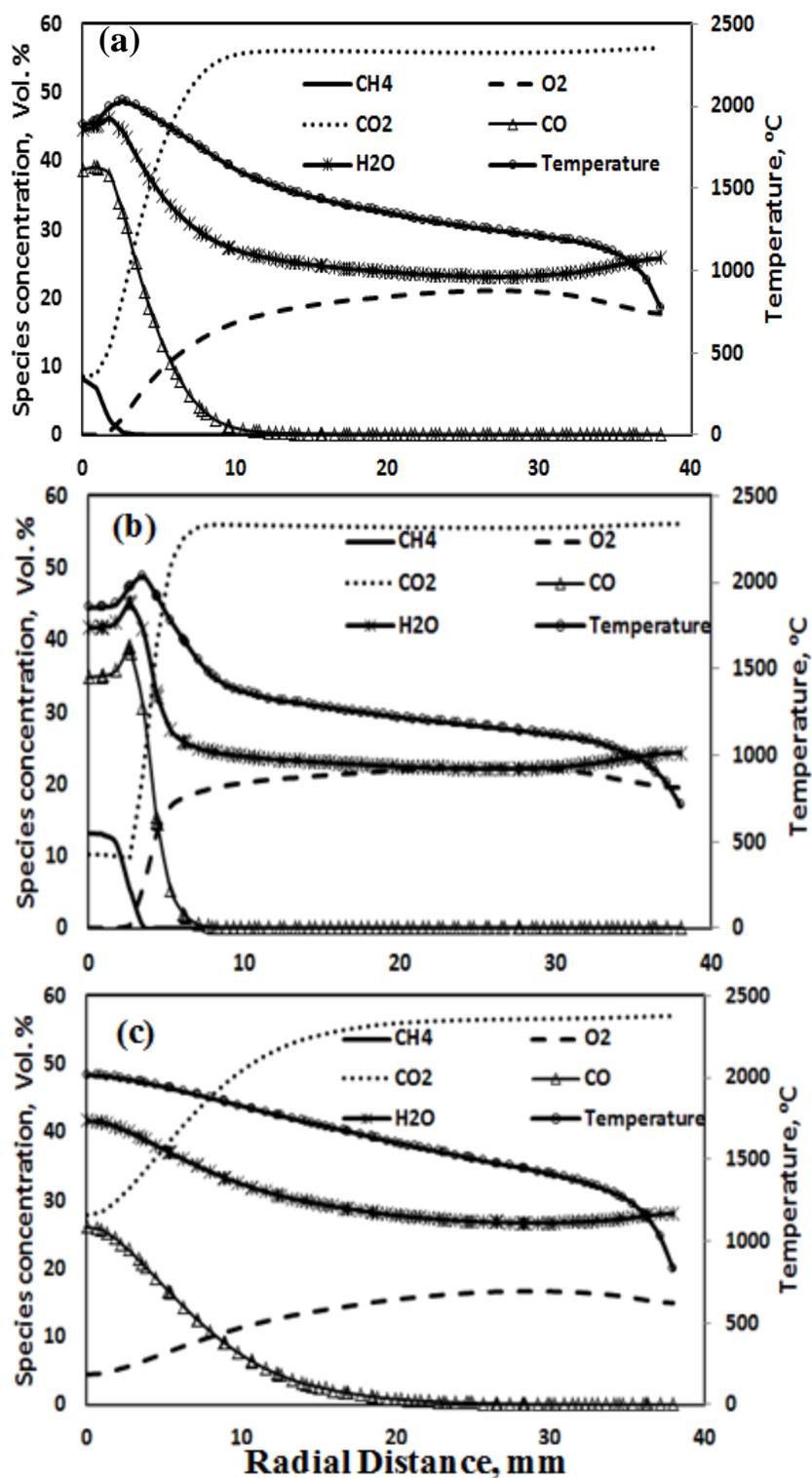


Figure 5.10 Predicted radial species concentration distribution and temperature at different reactor heights for $\Phi=0.65$, $V_f=6$ L/min and $O_2/CO_2:50/50\%$ (a) $h=25$ mm, (b) $h=50$ mm and (c) $h=100$ mm.

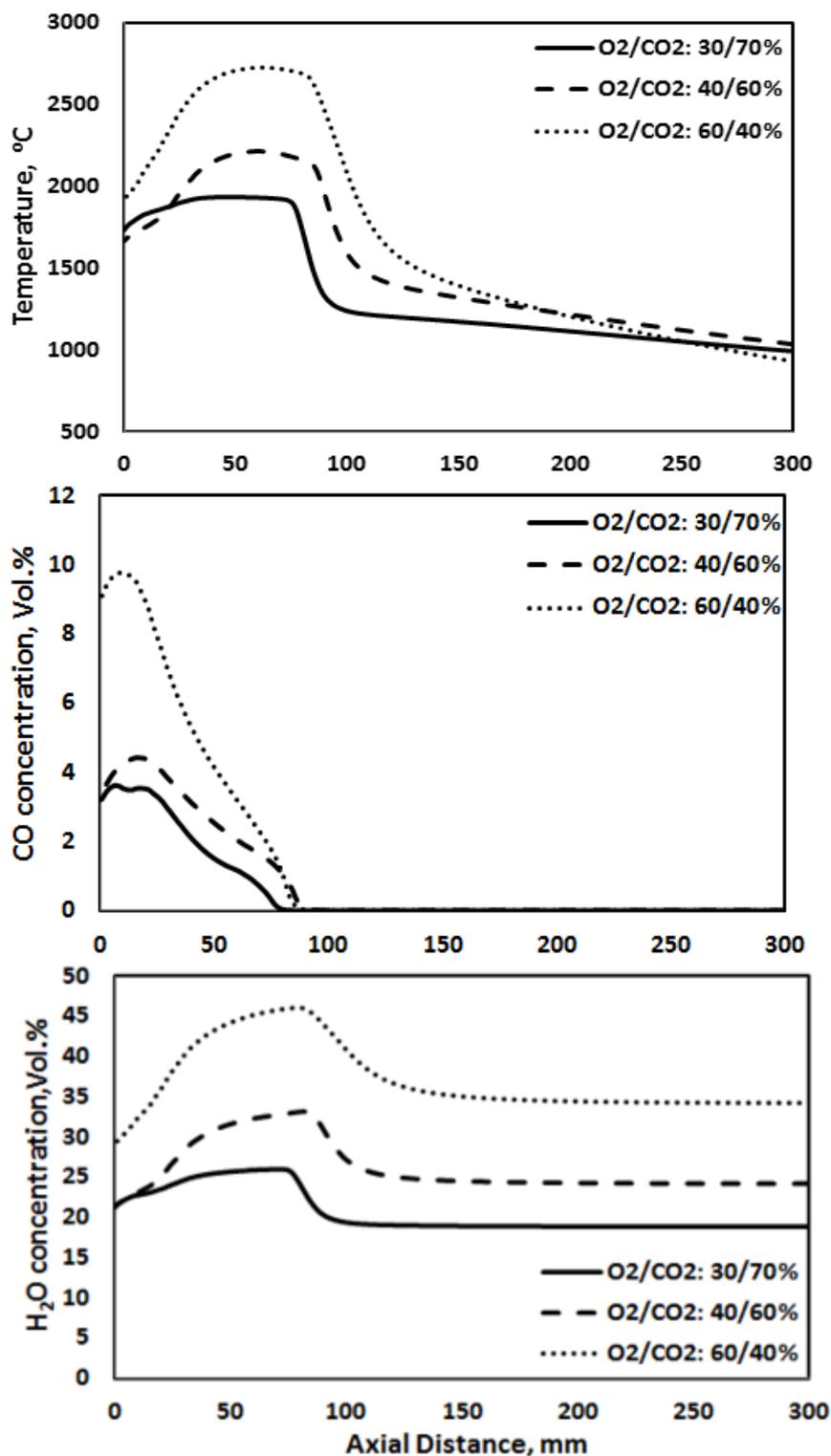


Figure 5.11 Predicted temperature, CO mole fraction and H₂O mole fraction distributions in the axial direction at different operating percentages of O₂/CO₂ in the oxidizer for $\Phi=0.65$ and $V_f=6$ L/min.

The contour plots of the distributions of the mole fractions of O_2 , CO and H_2O are presented in Fig.5.9 a and b at the x-symmetry plane of the reactor at $V_f=6$ L/min and $O_2/CO_2:50/50\%$ for two different equivalence ratios. As shown in Fig.5.9, the distributions of mole fractions of CO exhibit the highest values close to the fuel nozzle. The consumption of CO with increasing distance from the nozzle is in general accordance with the decrease in temperature as shown from the axial distributions in Fig.5.11. CO disappears after a certain height of the reactor, around $h=100$ mm. This is due to the consumption of CO in the reaction with O_2 to produce CO_2 and due to the extended reactor length which enables good gases mixing, no CO is found in the exhaust gas region.

From Figs.5.9 and 5.10, as the equivalence ratio increases as the amount of CO increases and this is due to the less availability of oxygen to complete the combustion. Also, as the percentages of Oxygen increases in the mixture, the rate of production of CO increases in the inner recirculation zone as CH_4 first combust and produce CO and then CO is consumed in the combustion with O_2 . For the O_2 concentrations, the larger concentrations are at inlet and in the outer recirculation zone and it decreases as the combustion proceeds. Less oxygen is available as the equivalence ration is increased away from the burner exit as expected. The shapes of the distributions of mole fractions of H_2O resemble strongly those of temperature for each flame in the same figure, Fig.5.9. This result is also confirmed from the axial distributions of both temperature and H_2O mole fractions in Fig.5.11. One can see that the larger concentrations of H_2O are near to

the combustion zone as the H_2O is a product of combustion and its concentrations are increased with increasing the amount of oxygen in the oxidizer mixture.

To configure more the species concentrations, radial gas concentration profiles for CH_4 , O_2 , CO , CO_2 and H_2O are shown in Fig.5.8 at different reactor heights for $\Phi=0.65$, $V_f=6$ L/min and $\text{O}_2/\text{CO}_2:50/50\%$. The considered heights in this figure represent the most intense combustion zone with the highest temperatures for all cases. CH_4 is consumed in the direction from center line to the reactor wall because of reactions with the incoming fresh gas and it completely disappears after $h=50\text{mm}$ due to the excess oxygen which is available to complete the combustion of CH_4 . Similar behavior to that of CH_4 is found for the distribution of CO inside the reactor as CO is an intermediate product and it disappear due in case of excess oxygen availability in the combustion zone. H_2O is maximum in the flame zone and it is reduced in the radial direction because of the reduced reaction intensity and increased concentrations of CO_2 because of coming fresh gas inlet. O_2 and CO_2 concentrations are maximum close to the reactor wall due to fresh gas inlet (O_2+CO_2) and decreases in the direction of the flame zone

5.5 Heat transfer

Figure 5.12 shows the axial distribution of reaction-1 Arrhenius rate at different operating conditions including percentages of O_2/CO_2 in the oxidizer at $\Phi=0.65$ and $V_f=6$ L/min, equivalence ratios at $V_f=6$ L/min and $\text{O}_2/\text{CO}_2:50/50\%$ and fuel volume flow rates at $\Phi=0.65$ and $\text{O}_2/\text{CO}_2:50/50\%$. As it is clear from the figure, part (a), when the percentage of O_2 in the oxidizer mixture is increased, the rate of reaction is also increases. This is

due to the existence of enough amount of oxygen to complete the conversion of CH_4 and as a result the reaction-1 rate will be increased and also reaction-2 rate is increased. This figure explains more the temperature profiles which have maximum values in the points of maximum rate of reaction.

It is shown that the rate of reaction reaches to nearly 5, 20 and 50 $\text{kg}\cdot\text{mol}/\text{m}^3\cdot\text{s}$ for percentages of O_2 of 30, 40 and 60, respectively and drops along the length of the reactor. The rate of reaction becomes zero after a certain height of the reactor and this is due to the fact that the fuel is totally consumed. Also, the rate of reaction-1 decreases as the equivalence ratio is increased due to the reduced available amount of oxygen to enhance the reaction. In addition to, the rate of reaction-1 is also increasing sharply when the amount of fuel volume flow rate is increased at the same operating equivalence ratio.

Reactor wall temperature profiles in the axial direction at different operating parameters are shown in Fig.5.13. due to improved combustion by increasing the amount of oxygen in the fresh gas mixture, the gas temperature inside the reactor increases and reaches its maximum values around $h=100\text{mm}$. as a result, the wall temperature is also increased as shown in Fig.5.13, part (a) and the total amount of heat flux across the reactor wall is also increased as shown in Fig.5.14, part (a). It was also found that the equivalence ratio has a significant effect on both wall temperature and accordingly the rate of heat loss across the reactor wall.

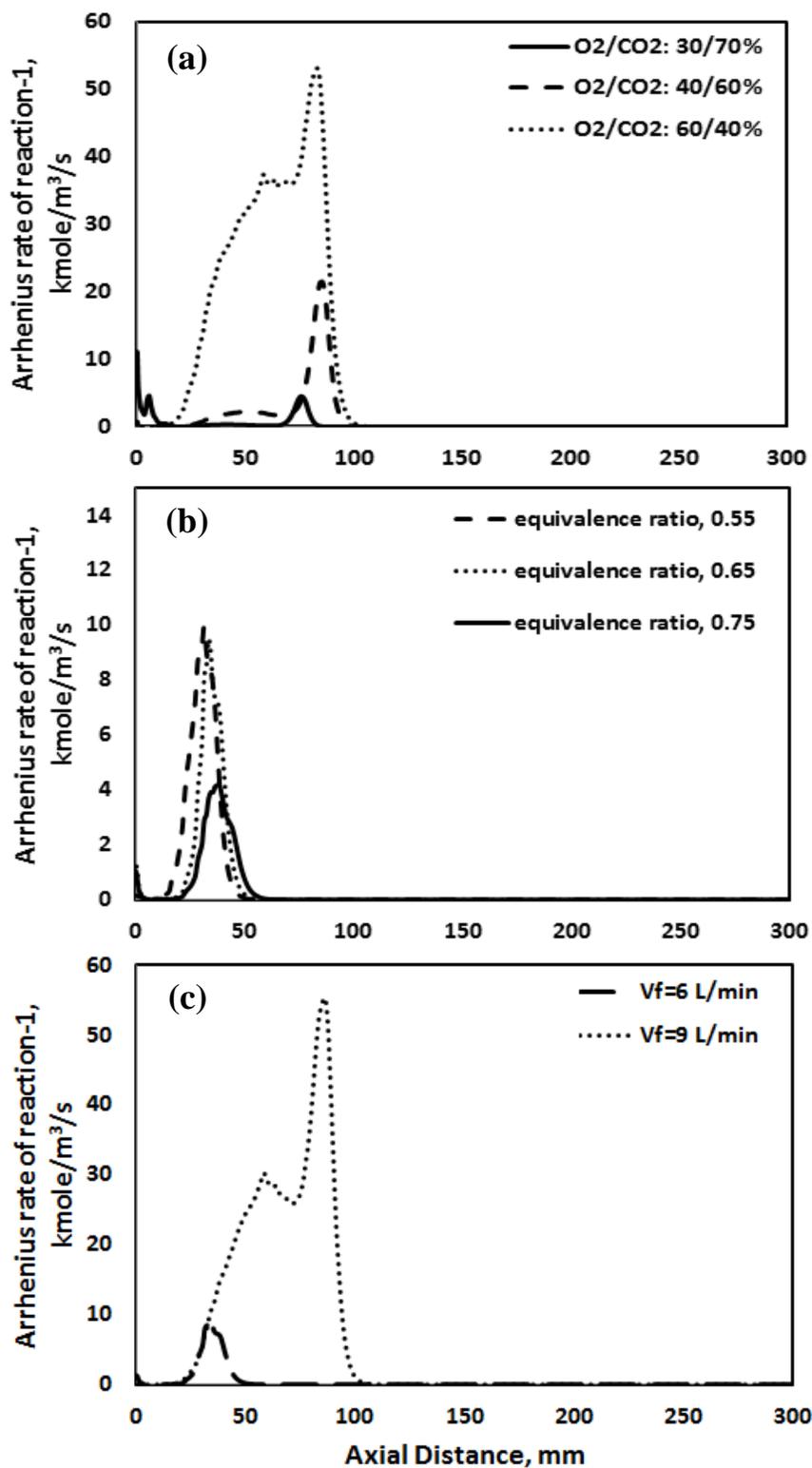


Figure 5.12 Predicted axial distribution of reaction-1 Arrhenius rate at different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and O₂/CO₂:50/50% and (c) $\Phi=0.65$ and O₂/CO₂:50/50%.

As shown in Figs. 5.13 and 5.14, part(b), both wall temperature and wall heat flux are decreased with decreasing the equivalence ratio. This can be attributed to the cooling effect of the increased amount of the oxidizer that enters the reactor with decreasing the equivalence ratio. This amount helps in cooling the gases close to the reactor wall and then decreases the amount of total heat flux across the wall. In part (c) of both figures 5.13 and 5.14, one can observe the great differences in both wall temperature and wall heat flux as the amount of fuel volume flow rate is changed from 6 to 9 L/min at the same operating equivalence ratio. Increasing the fuel flow at the same equivalence ratio results in increase in the amount of oxidizer and improved flow swirl. As a result, the overall mixing and combustion process are improved causing a significant increase in the combustion temperature. Because of this improved performance, the wall temperature increases and accordingly the amount of heat flux across the reactor wall increases.

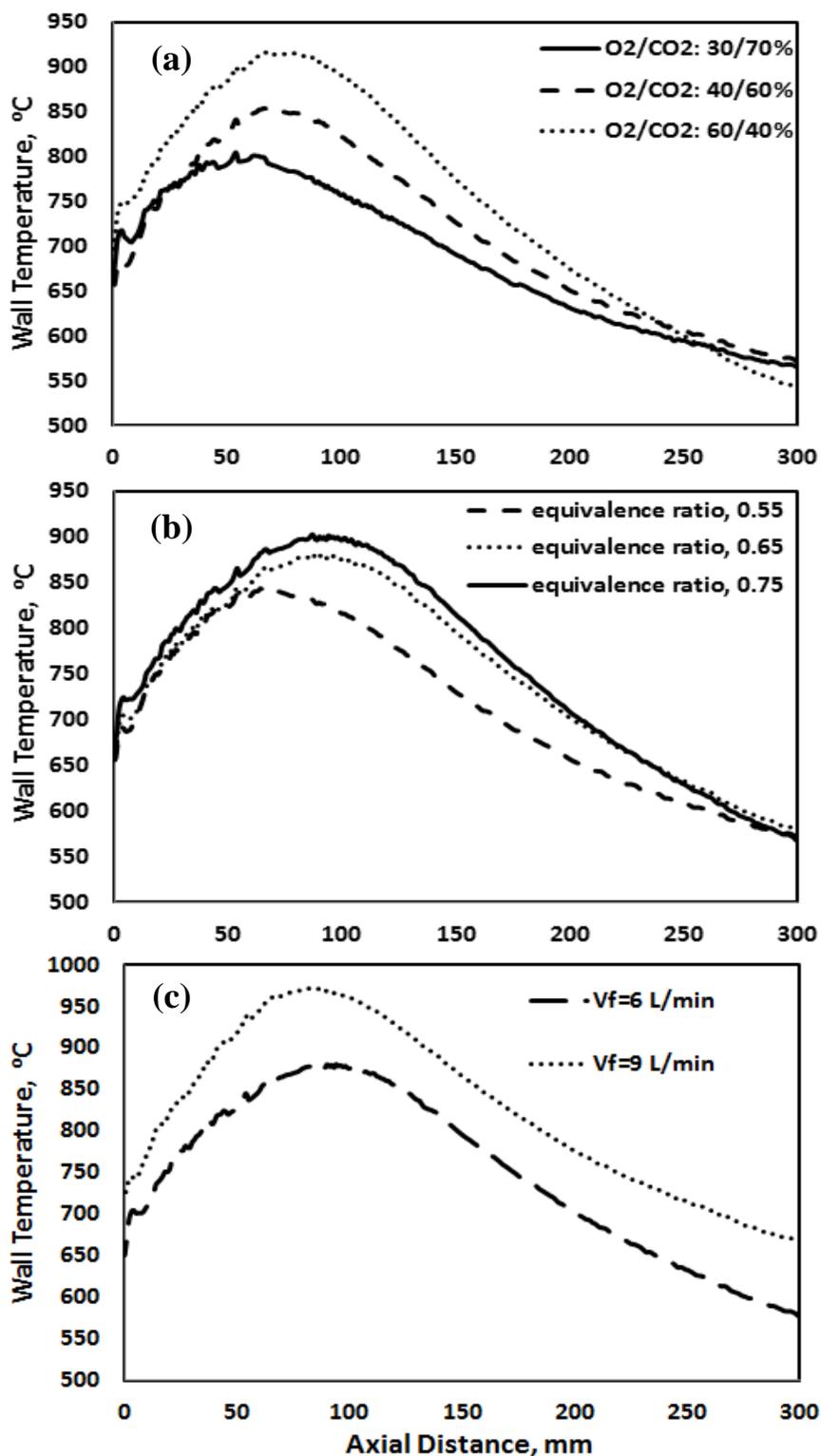


Figure 5.13 Predicted reactor wall temperature distribution in the axial direction at different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and O₂/CO₂:50/50% and (c) $\Phi=0.65$ and O₂/CO₂:50/50%.

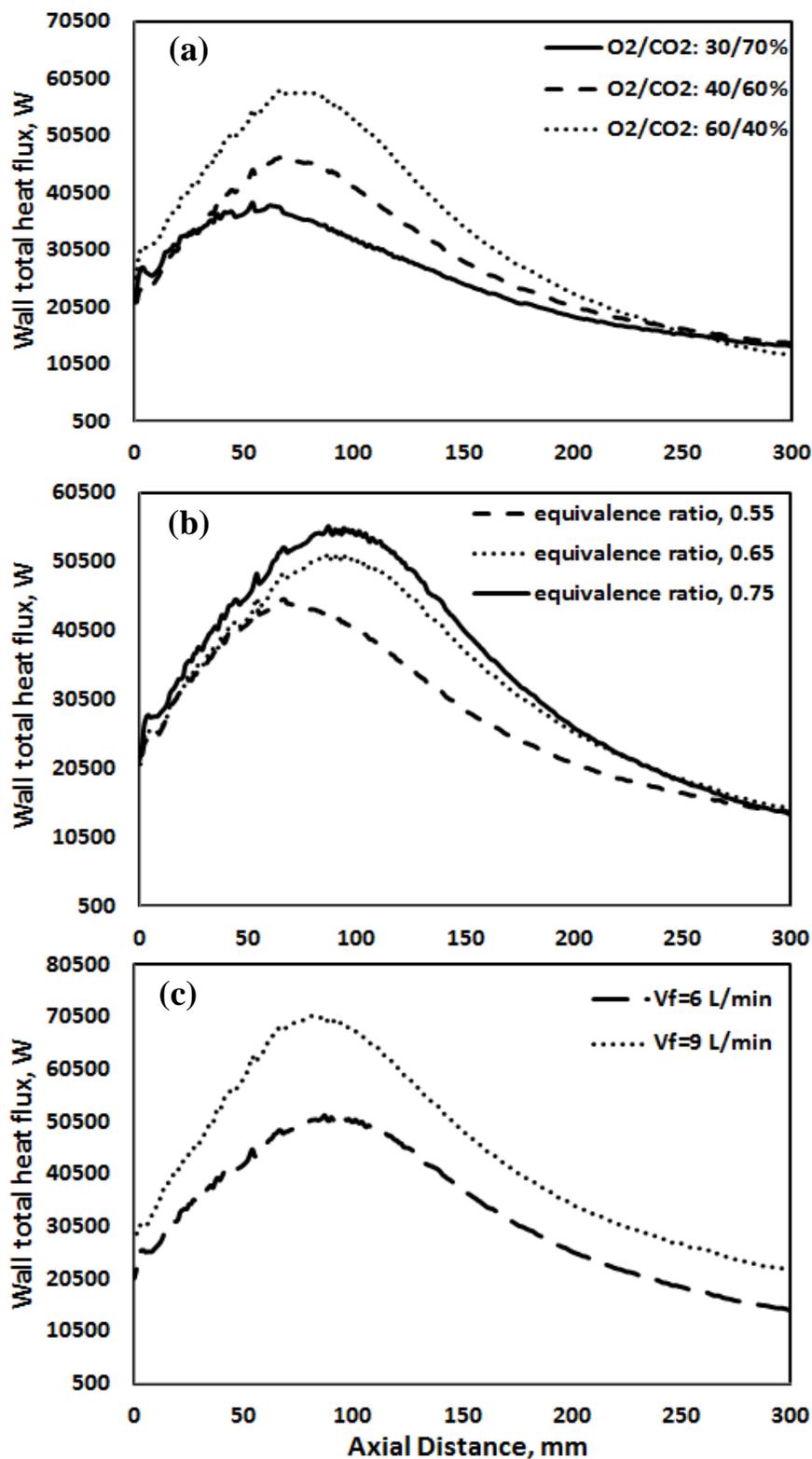


Figure 5.14 Predicted reactor wall total heat flux distribution in the axial direction at different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and O₂/CO₂:50/50% and (c) $\Phi=0.65$ and O₂/CO₂:50/50%.

5.6 Comparison between measured and calculated exhaust temperature and emissions

Figure 5.15 shows a Comparison between experimental and numerical exhaust radial gas temperature at $h=300$ mm at different operating conditions as shown in the figure. For CH_4/oxy -combustion, the flames were subject to thermo-acoustic instabilities over a substantial range of operating conditions. As shown in Fig.5.15, part (a), the exhaust gas temperature increases at the same radial position with increasing O_2 content in the oxidizer mixture from 30 to 40%. This is attributed to the higher flame temperature which causes an increase in the reactivity leading to higher laminar flame speeds and shorter ignition delay times.

When the percentage of O_2 in the mixture is increased to 60%, the exhaust temperature was reduced again. From the experimental work conducted for all ranges of the flames, the flame lift starts to occur when the O_2/CO_2 ratio in the mixture reaches 50/50%. Further reduction in the percentage of O_2 in the mixture (increasing CO_2) leads to an increase in the flame lift and significant influences on the combustion intensity and stability. This flame lift off may be due to the smaller diameter of the fuel nozzles however the height of the flame lift off is reduced because of the divergent shape of the oxidizer gases inlet section and the creation of the outer recirculation zone. Due to the increased flow velocity by increasing the mass flow rates, the residence time for combustion is increased as a result of delayed mixing between gases and fuel and the flame is moved away from the gases inlet sections. Also, fuel type which is gaseous fuel, Methane, may have also additional effects on the flame lift off. When the O_2/CO_2 ratio is 60/40%, flame

lift is not there as compared to the cases of 30/70% and 40/60% and that's why the exhaust temperature in case of 60/40% is less than the other considered cases in Fig.5.15, part (a). The temperature is maximum at the centerline and decrease toward the reactor wall. The change in chemical reaction rates along with the reduced Reynolds numbers are expected to be main causes for the change of the flame structure when changing the percentage of oxygen in the oxidizer mixture.

To investigate the effect of equivalence ratio on the exhaust gas temperature, Fig.5.15-part(b) is showing this effect at $V_f=6$ L/min and $O_2/CO_2:50/50\%$. At the same fuel volume flow rate, the amount of corresponding oxidizer is lowered when the equivalence ratio is increased and the availability of Oxygen is also reduced. This may justify the lowered exhaust gas temperature when the equivalence ratio is increased as shown in the figure from both experimental and numerical temperature data. The flow swirl is a very important parameter and it forces the flow beside the wall to go toward the flame zone. By lowering the oxidizer flow (increasing equivalence ratio) the swirl will be affected and a large portion of the oxidizer will escape beside the reactor wall without participating in the combustion process. That's why the temperature is reduced by increasing the equivalence ratio toward stoichiometry.

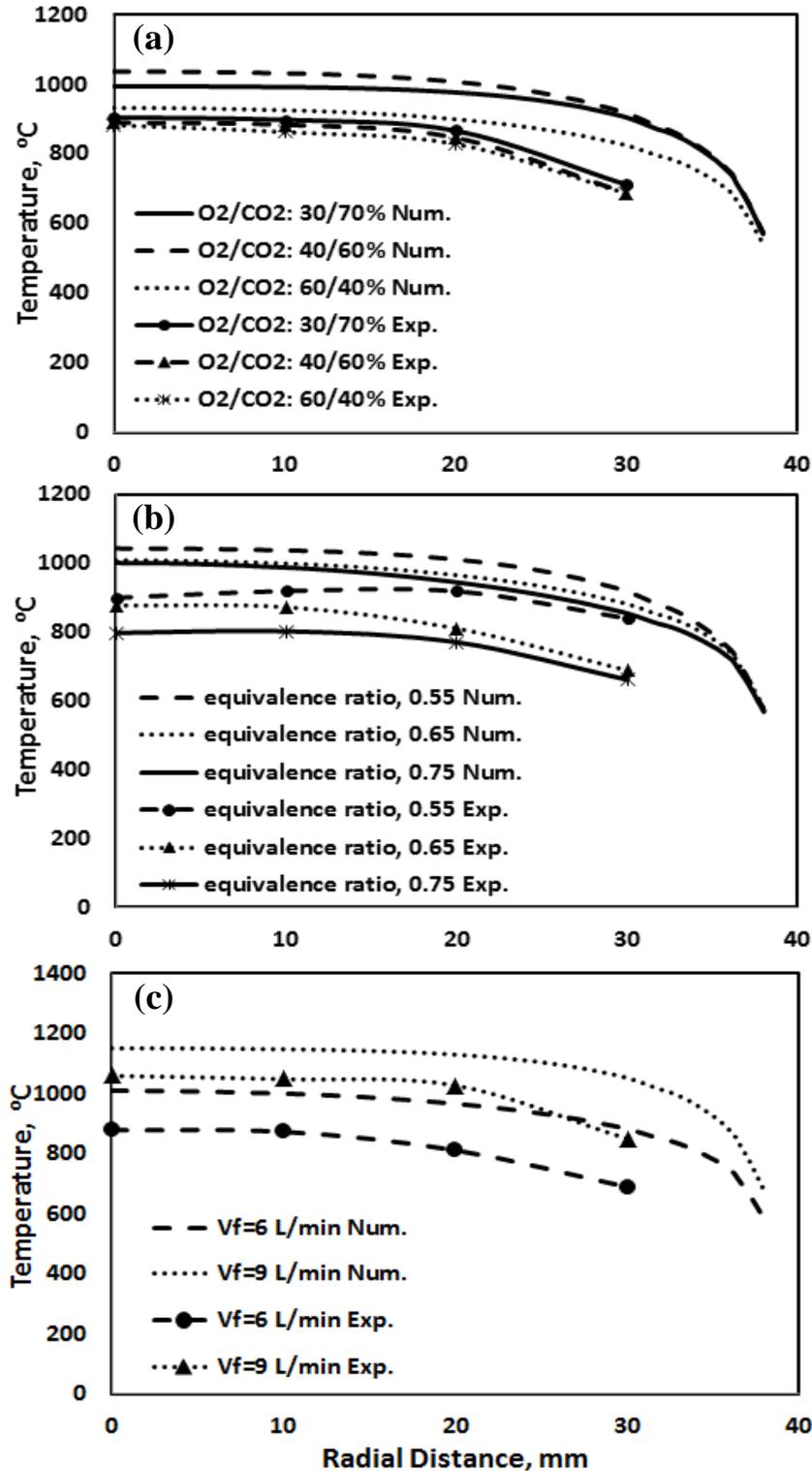


Figure 5.15 Comparison between radial experimental and numerical exhaust gas temperature at $h=300$ mm at different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and $O_2/CO_2:50/50\%$ and (c) $\Phi=0.65$ and $O_2/CO_2:50/50\%$.

In part(c) of Fig.5.15, the effect of fuel volume flow rate on the combustion temperature is investigated at fixed equivalence ratio and O_2/CO_2 ratio. As seen, increasing the fuel flow at fixed equivalence ratio improves the overall combustion process and so, the exhaust gas temperature is also improved. As shown in the figure, both experimental and numerical results are in a slightly good agreement. This deviation between experimental and numerical data may be attributed to slight movement of the temperature probe inside the reactor in addition to the error comes from the reading of the thermocouple probe itself. There may be also some errors in the calculations of the CO_2 concentrations that directly affect the temperature distribution inside the reactor. In the present study, only two step reaction kinetics model has been considered which is a small number of steps in order to consider most of the intermediate species. However, because of the calculation time considering the 3D simulations, the present two step model has been used with expected reasonable errors in the calculations as compared to higher number of steps models.

A Comparison between experimental and numerical average exhaust gas emissions at $h=300$ mm as a function of percentage of O_2 in the oxidizer mixture, equivalence ratio and fuel volume flow rate is shown in Fig.5.16. Due to the long length of the combustor, the combustion is almost complete and no CO is appearing there experimentally and numerically as shown in the figure. As shown in Fig.5.16, part(a), the concentration of CO_2 in the exhaust gas is reduced when the amount of O_2 is increased in the oxidizer mixture which consists of O_2 and CO_2 . However, by increasing the amount of oxygen, the combustion process is improved and CO_2 created by combustion is increased. But, the effect of CO_2 reduction in the oxidizer mixture is greater than the effect of increase of

CO₂ due to improved combustion. As expected, the concentration of H₂O is increased in the exhaust by increasing O₂ in the oxidizer mixture due to the improved combustion process as H₂O is a combustion product. Also, O₂ concentrations are increased as shown in the figure. By increasing the equivalence ratio at fixed ratio of O₂/CO₂% and fuel volume flow, the concentrations of CO₂ and O₂ are decreased and H₂O concentrations are slightly increased. By increasing the fuel volume flow rate at a fixed operating equivalence ratio and O₂/CO₂%, the concentrations of all species are not affected much as shown in Fig.5.16, part(c).

In conclusion for this portion of the present work, both experimental and numerical investigations were conducted for an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor. Oxy-combustion and emission characterization, flame stabilization and oxy-combustion model validation have been investigated in details. The combustor is fuelled with CH₄ and a mixture of CO₂ and O₂ as oxidizer. A modified two-step oxy-combustion reaction kinetics model for methane-oxygen combustion has been used in order to predict the oxy-combustion characteristics of the considered flame and validations have been done using the experimental results. Wide ranges of different operating parameters have been considered including equivalence ratio, percentage of O₂/CO₂ in the oxidizer mixture and fuel volume flow rate. The stability of the oxy-combustion diffusion flame has been checked experimentally and numerically.

From the above results, one can conclude that the stability of the oxy-combustion flame is affected when the operating percentage of Oxygen in the oxidizer mixture is reduced below 25 %. In addition to, no operation was possible for the burner with less than 21% Oxygen in the oxidizer mixture. Visualizations of the flame at the above mentioned operating conditions have been carried out experimentally and comparisons with the numerical results have been done. The flames have been characterized in details by measuring the exhaust gas temperatures and emissions and comparing them with those from the numerical model. The combustion stability was found to be improved with increasing the percentage of O₂ at inlet however there is a limitation in temperature. Also, by lowering the equivalence ratio, improvement in flow swirl and the overall combustion process has been reached. Both experimental and numerical results are in good agreement and the modified two step reaction kinetics model is capable of predicting very similar trends of temperature and also the overall flame shape is very close to the recorded experimental shapes.

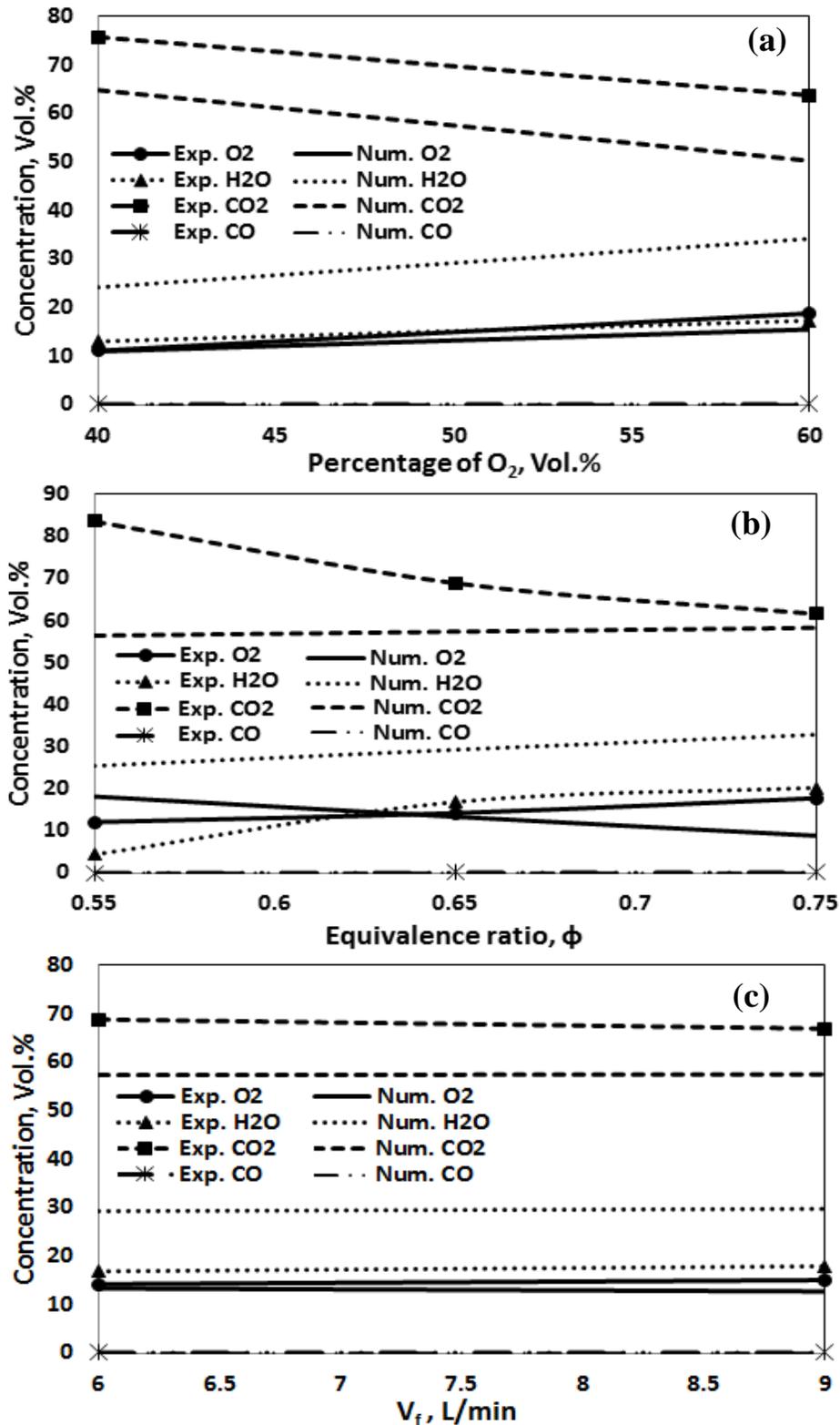


Figure 5.16 Comparison between experimental and numerical average exhaust gas emissions at $h=300$ mm as a function of different operating parameters: (a) $\Phi=0.65$ and $V_f=6$ L/min, (b) $V_f=6$ L/min and O₂/CO₂:50/50% and (c) $\Phi=0.65$ and O₂/CO₂:50/50%.

CHAPTER 6

RESULTS AND DISCUSSIONS OF THE 2D SIMULATIONS

OF THE ITM REACTOR

In the present work, the modified two step finite rate oxy-combustion reaction kinetics model done by Andersen et.al. [29] is used to predict a oxy-combustion characteristics inside a stagnation flow ITM reactor. A detailed study is presented here to understand more the performance of ion transport membranes under the oxy-combustion conditions in the permeate side of the membrane. Effects of many parameters including inlet gases temperature, reactor geometry, feed and sweep flow rate, oxygen partial pressure in the feed side and the effect of the percentage of CH₄ in the sweep gases mixture on the permeation and combustion processes are included in this work.

Due to the symmetry in the computational model, only half part of the domain is considered and all the line plots in Y-direction are at the symmetry line. The symmetry line length located inside the feed zone is 3cm and it is fixed in all simulations; however, the symmetry line part located inside the permeate zone starts from membrane surface (Y=3cm) and it was varied in a set of simulations to see the effect of geometry on permeation process otherwise it was fixed and equal to 3cm.

6.1 validation of the 2D model

Figure 6.1 compares the present model results with the experimental data of the previous literature work of Xu and Thomson [130] to investigate the effect of oxygen partial pressure in the permeation side on the overall oxygen permeation flux. To do this validation, a new mesh was developed to simulate the membrane reactor in their study and the present numerical model was applied to this computational domain. Change of oxygen partial pressure in the permeation side has been done through the change of the nitrogen flux coming in the sweep/purge gas in the permeate side from 4 to 120 ml/cm².min. As shown from Fig.6.1, both experimental and numerical data are in a good agreement. Also, as it is clear from the graph, the partial pressure of Oxygen in the permeate side decreases as the oxygen permeation flux increases. This is due to the increased pressure gradient across the membrane at constant oxygen partial pressure in the feed side.

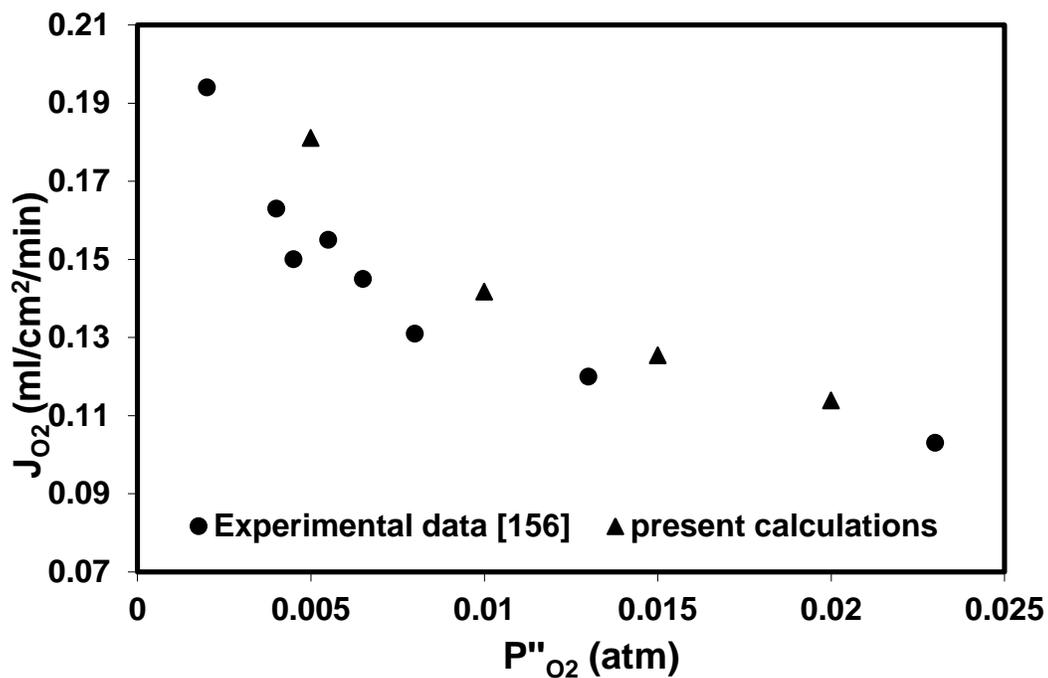


Figure 6.1 Effect of the permeate side oxygen partial pressure on the oxygen permeation flux for both experimental data [156] and the present calculations at

$P'_{O_2}=1$ atm and N_2 flux=4-120 ml/cm²/min.

6.2 Inert operations (separation only)

In this part of the present work, argon is used as an inert sweep gas to flow inside the permeate zone to extract oxygen through the membrane in the absence of fuel (no reactions). In this part, investigations of the dependence of oxygen permeation flux on the gases inlet temperature and accordingly the membrane temperature without considering reactions inside the permeate zone have been done. As shown in Fig.6.2, the permeation oxygen flux is very sensitive to the membrane temperature and increases sharply as the temperature increases. This is due to the reduced surface exchange resistance to oxygen permeation as the temperature increase. Also, as the membrane temperature increases as the movement of the gases on the surface of the membrane inside the permeate zone increases causing a reduction in the oxygen partial pressure in the permeate side and hence increasing the driving force for oxygen permeation across the membrane. However, the activation energy for the two surface reaction rates and the oxygen vacancies diffusion will be affected by temperature increase and may the dependence of oxygen flux on membrane temperature be reduced at a certain temperature.

The effect of membrane temperature on the oxygen partial pressure in feed and permeate sides of the membrane is shown in Fig.6.3. As shown in the figure, as the partial pressure of oxygen inside the feed zone decreases near to the membrane surface as the temperature increases reflecting higher oxygen flux due to higher driving force across the membrane and reduced permeation resistance. As a result of increased oxygen permeation flux, the oxygen partial pressure inside the permeate zone was increased.

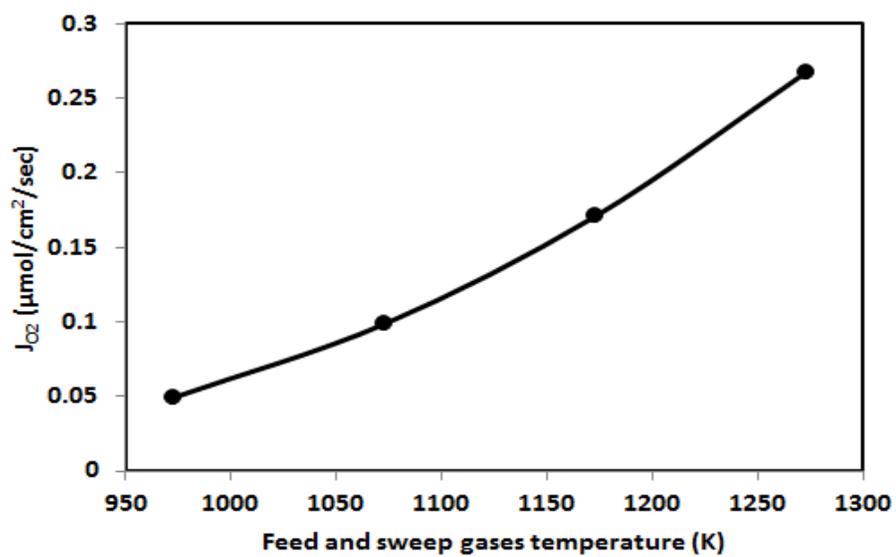


Figure 6.2 Oxygen permeation flux as function of feed (air) and sweep (argon) gases inlet temperature at feed and sweep gases volume flow rate of 500 sccm and $P_{O_2}=0.21$ atm.

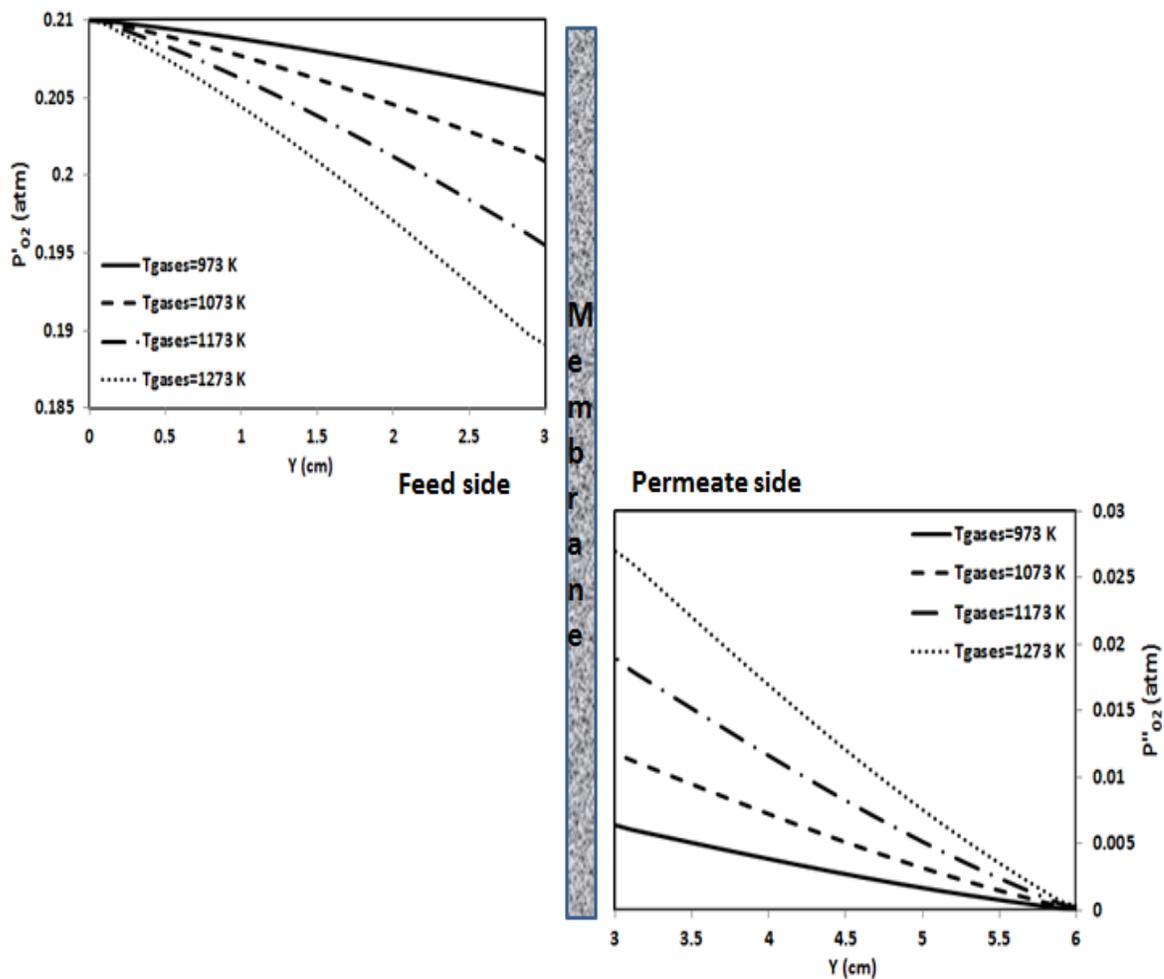


Figure 6.3 Oxygen partial pressure in feed and permeate sides of the membrane as function of feed (air) and sweep (argon) gases inlet temperature at feed and sweep gases volume flow rate of 500 sccm and $P_{O_2}=0.21$ atm.

6.3 Effect of radiation heat transfer

The importance of thermal radiation in heat transfer mechanism in ITM reactors systems has been well identified in the past few years. In the present study, the effects of radiation heat transfer on oxy-fuel combustion characteristics in the permeate side of the 2D ITM reactor are investigated. Effects of reaction heat transfer on combustion temperature and reaction 1 rate at 2.5/97.5% Vol. CH₄/CO₂ as sweep gases, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and P_{O₂}=0.21 atm are shown in Fig.6.4. The discrete ordinates radiation model is used to predict the radiation heat transfer. As shown in Fig.6.4, it is observed that excluding radiation model results in the over-prediction of combustion temperatures in the membrane reactor. It is also observed from part (2) in Fig.6.4 that the overall reaction rate and its peak value increase when accounting for radiative heat transfer, despite the decrease in temperature caused by radiation. Therefore, it is important to incorporate a radiation heat transfer model in combustion inside ITM reactors in order to predict their characteristics accurately. That's why, in all of the membrane reactor results, discrete ordinates radiation model has been applied in order to provide more accurate results.

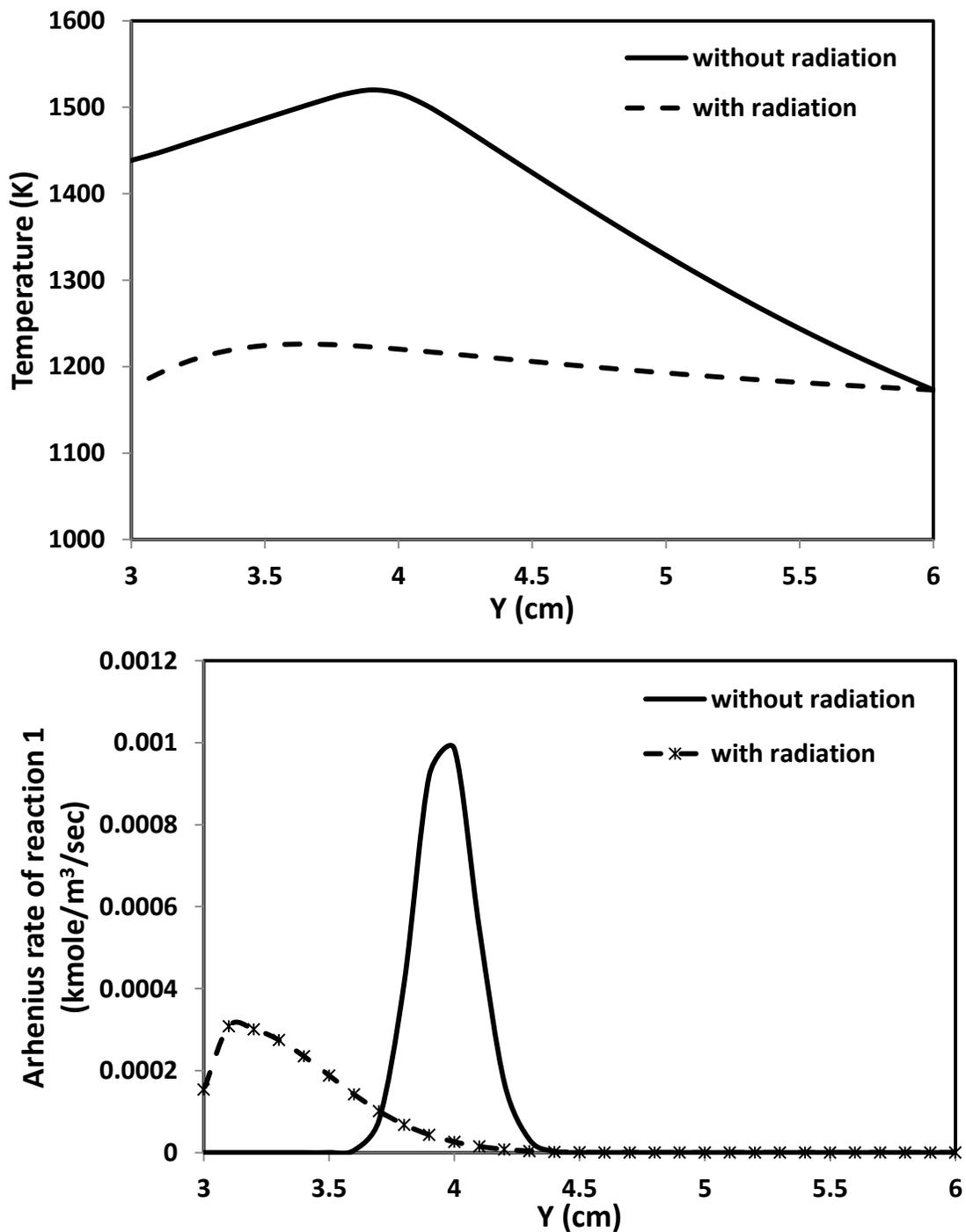


Fig.6.4 Effects of reaction heat transfer on temperature and reaction 1 rate at 2.5/97.5% Vol. CH₄/CO₂ as sweep gases, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and P_{O₂}=0.21 atm.

6.4 Effect of reactivity

In this work, the sweep gases used are CO_2 and CH_4 in order to investigate the reactive ITMs. CO_2 is used instead of argon due to reduced oxygen flux using argon as compared to CO_2 as shown in Fig.6.5. In all of oxy-combustion applications, the main target is to capture CO_2 easily without any extra separation processes that will be needed in case of using argon as an energy carrier medium in case of reactive applications. Also, in all of the carbon free operations, the carbon dioxide is already available in the exhaust so, it could be recirculated and used as sweep gas and energy carrier without any additional costs. As one can see from Fig.6.5, the percentage of CH_4 increases in the sweep gases mixture as the amount of oxygen flux permeation increases for both cases of mixing operation (no reacting) and the reacting medium operations; however the increase is sharp in case of reactions are activated. It was found that the permeate side conditions and the chemical reactions have significant effects on the oxygen permeation flux.

Figure 6.5 also shows the influence of reactivity on oxygen permeation flux for different concentrations of CH_4/CO_2 . As shown in the figure, the oxygen permeation flux is increased with activating the reactions in the permeate side of the membrane. This is due to the increase in membrane temperature because of combustion and also the reduced oxygen partial pressure due to the consumption of oxygen in the combustion process. Figure 6.6 is confirming those analysis as we have large reduction in the oxygen partial pressure inside the permeate zone for the reacting cases as compared to the cases without activating reactions in the calculations. Also, the oxygen flux increases sharply with

activating reactions in the permeate side, the oxygen partial pressure inside the feed zone is reduced also sharply as compared to non-reacting cases. Also for reacting cases, the heat generated by combustion is transferred to the feed zone through the membrane surface causing an increase in the membrane temperature and also increased air temperature near to the membrane surface in the feed zone causing more oxygen flux.

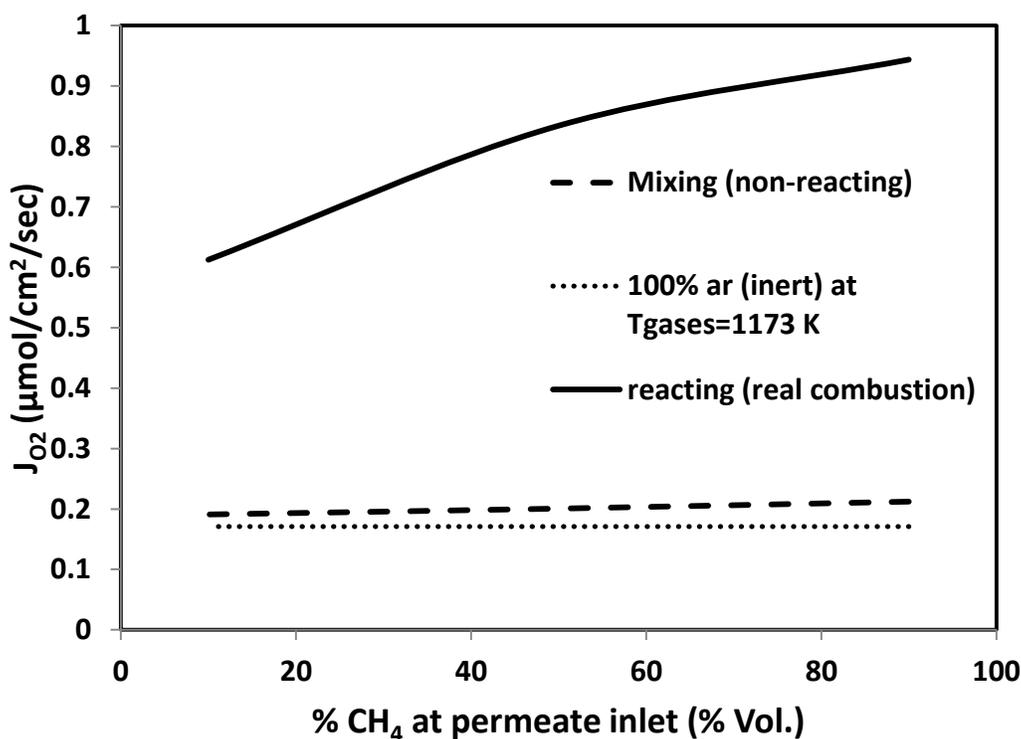


Figure 6.5 Effect of reactivity on oxygen permeation flux for different percentages of CH_4/CO_2 as sweep gases at feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}=0.21\text{ atm}$.

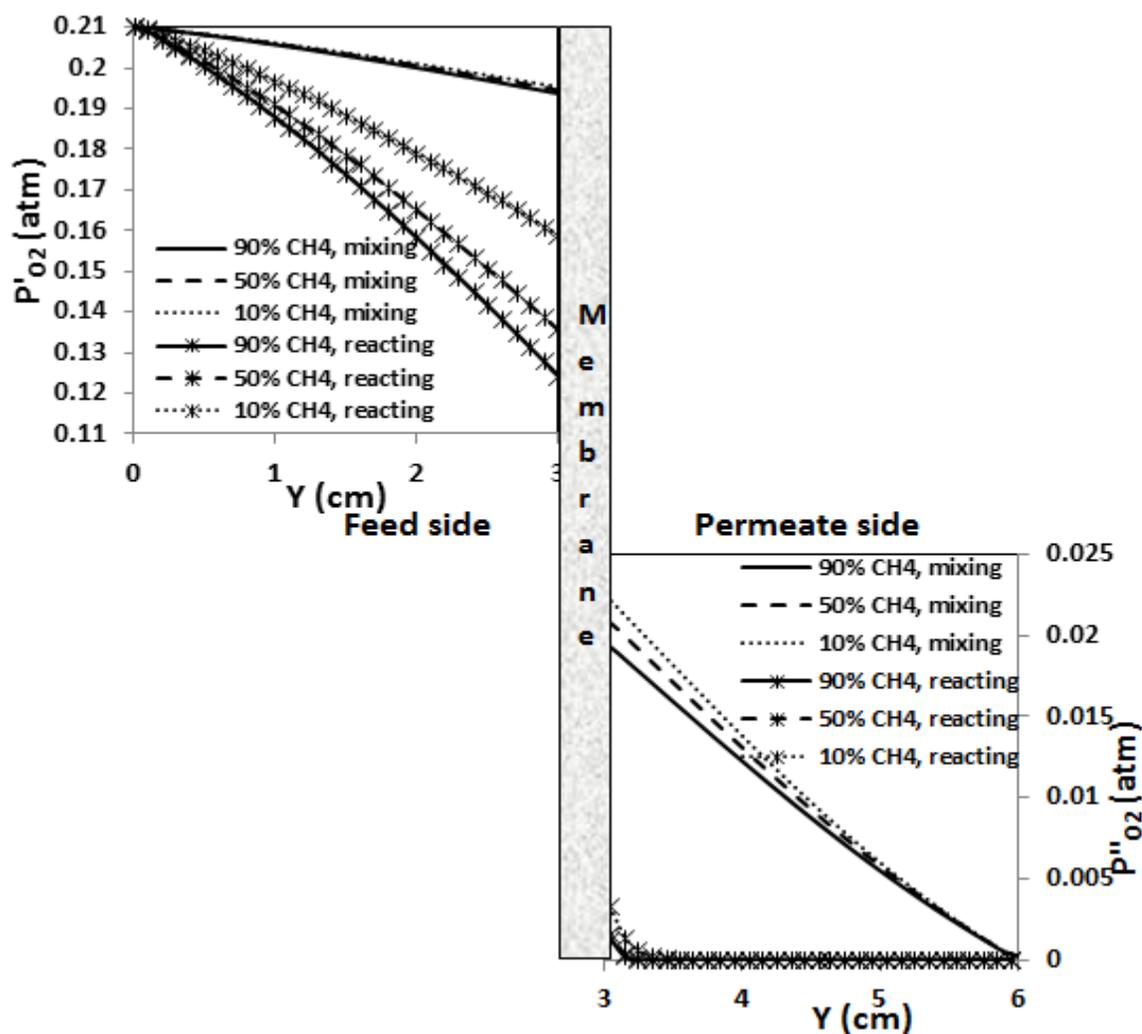


Figure 6.6 Effect of reactivity on oxygen partial pressure in both sides of the membrane for different percentages of CH₄/CO₂ as sweep gases at feed and sweep gases volume flow rate and inlet temperature of 500 scm and 1173 K respectively and $P_{O_2}=0.21$ atm.

To see more complete view for the oxygen partial pressure distribution inside the whole reactor and compare both cases of reacting and non-reacting mediums, Fig.6.7 is showing the contour plots of oxygen partial pressure inside the whole reactor for 5/95% Vol. as sweep gases mixture, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}=0.21$ atm. As shown in part (a) in the figure for the mixing only case (non-reacting), oxygen molecules exist in the whole permeate zone however in part (b), the oxygen is completely consumed inside the permeate zone due to its consumption in the combustion process. There is larger gradient in oxygen concentration near to the membrane surface in the feed zone due to increased oxygen permeation in case of reacting medium compared to mixing only case.

6.5 Oxy-combustion characteristics

In the rest of the present work, the influences of many parameters (including effect of sweep CH_4/CO_2 ratio, Effect of inlet temperature, effect of geometry, effect of feed and sweep volume flow rates and effect of oxygen partial pressure inside the feed zone) on the oxygen permeation process and oxy-combustion characteristics are investigated relative to our base case (5/95% Vol. CH_4/CO_2 as sweep gases, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}=0.21$ atm). In the present section, the oxy-combustion characteristics are investigated based on our base case in this study. Fig.6.8 shows the contour plots of: (a) temperature, (b) mole fractions of H_2O , (c) mole fractions of CH_4 and (d) mole fractions of CO in both sides of the membrane for the base case.

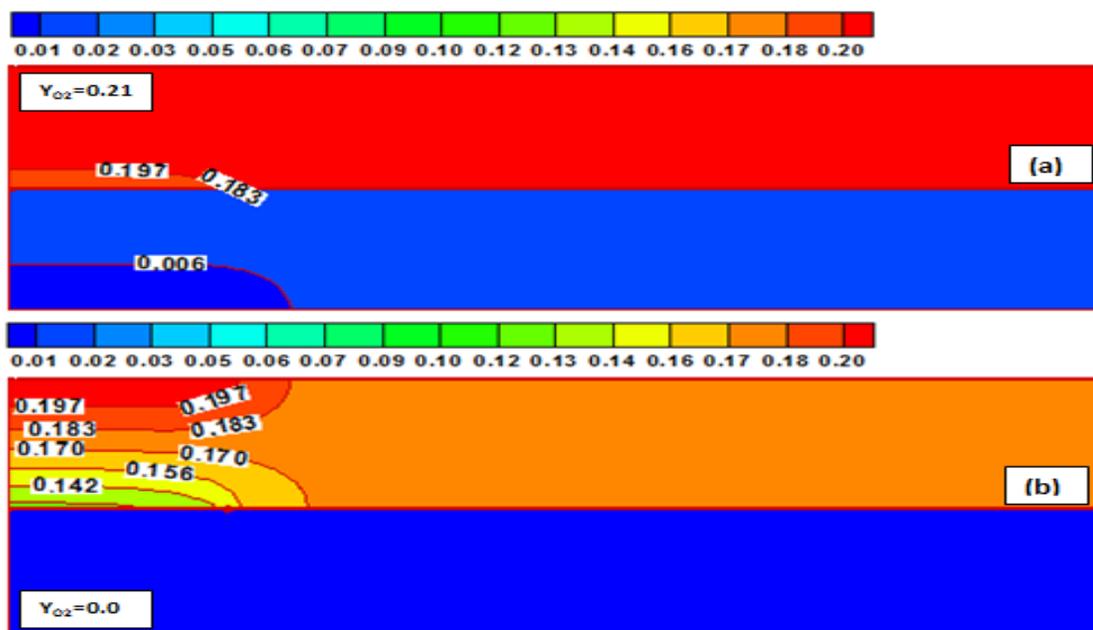


Figure 6.7 Contour plots showing the effect of reactivity on oxygen partial pressure in both sides of the membrane at 5/95% Vol. CH_4/CO_2 as sweep gases, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2} = 0.21$ atm.

As shown in part (a) from the contour plots of temperature, the reaction zone is close to the membrane surface and the maximum temperature is about 1217 °C inside the permeate zone. The values of mole fractions of CH₄, H₂O and CO (Y_{CH_4} , Y_{H_2O} and Y_{CO}) are equal to zero inside the feed side as shown in Fig.6.8. As the maximum temperature increases as the membrane temperature increases by heating from combustion zone; however, part of this heat will be lost to the air domain through the membrane surface causing a reduction in its temperature and also this heat lost to the air domain causes an increase in feed zone temperature near to the membrane surface and as a result, an increase in oxygen permeation flux will be encountered. Also it could be seen from the figure that the temperature distribution beside the membrane surface is uniform, this will extend the membrane working period and prevent membrane fracture due to thermal stresses on the membrane surface (idea of isothermal membrane reactor).

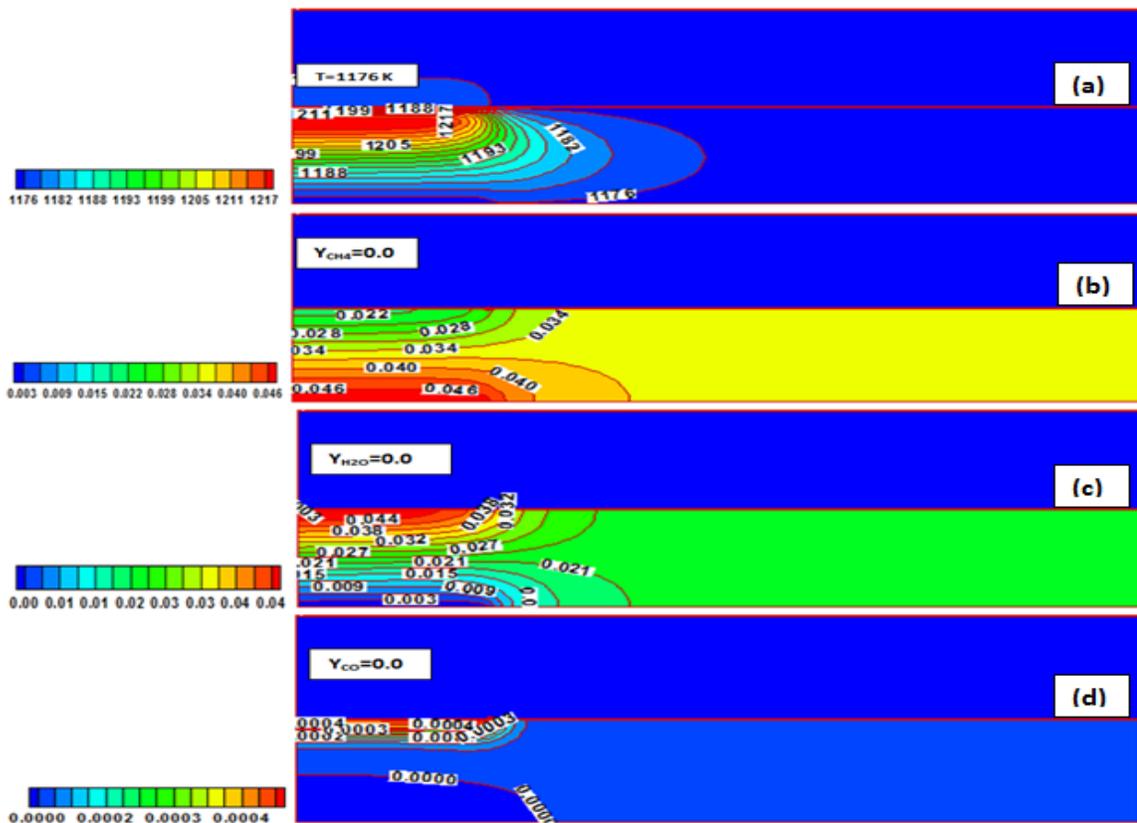


Figure 6.8 Contour plots of: (a) temperature, (b) mole fractions of CH₄, (c) mole fractions of H₂O and (d) mole fractions of CO in both sides of the membrane at 5/95% Vol. CH₄/CO₂, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}=0.21$ atm.

The reactions occur in the region close to the membrane surface where enough oxygen for combustion exists. However, away from the membrane surface, no enough oxygen for combustion will be available and so the reactions will be reduced. In part (b) of the same figure, Fig.6.8, the contour plots of mole fractions of CH_4 are shown. The concentration of CH_4 is reduced in the direction of membrane surface from the inlet of the sweep gases due to the consumption of CH_4 in the combustion process; however, no complete conversion of CH_4 is there because of not enough amount of oxygen permeation through the membrane and then not complete combustion and also because a great portion of the coming CH_4 from the inlet opening don't go to the flame zone. However, part of CH_4 due to the present design of the sweep gases inlet of the reactor escapes from the reaction region but, this design is very good for keeping the temperature constant (isothermal membrane reactor) through the membrane surface and prevents membrane fracture due to thermal stresses.

Part (c) in Fig.6.8 presents the contour plots of H_2O mole fractions. As a matter of fact, H_2O is a combustion product and its mole fractions should resemble strongly the contour plots of temperature distribution in the upper part of the figure. The area of maximum values of H_2O mole fractions is the same area of maximum temperature which is the reaction zone as H_2O is a product of the combustion process. The concentration of H_2O is high near to the membrane surface causing a reduction in partial pressure of O_2 in the close region to the membrane surface; this will result in increasing the oxygen permeation flux through the membrane. The last part of Fig.6.8 shows the contour plots of CO as intermediate combustion product however great part of the created CO will not

continue in the reaction due to lack of enough O_2 and hence incomplete combustion. Also the CO concentration is maximum inside the reaction zone.

The average values of the species mole fractions at the permeate zone outlet are 0.036125, 0.00163, 0.940327, 0.021872 and 0.000043 for CH_4 , O_2 , CO_2 , H_2O and CO respectively which are summing to the value of one indicating the accuracy of the calculations. To compare the values of species mole fractions in the same figure, Fig.6.9 shows the species mole fractions through the symmetry line inside the permeate zone. As shown, CH_4 and O_2 are disappearing in the reaction zone beside the membrane surface while H_2O , CO and CO_2 are increasing as they are combustion products. Because of very high values of CO_2 mole fractions as compared to the other species, it was removed from the figure to be able to see the other species clearly. Higher CO_2 concentrations are diffused from the reaction zone to the membrane surface and this may lead to reduced partial pressure of O_2 and as a result, the oxygen permeation flux may increase. The values of CO mole fractions are very low as compared to the other species as it is an intermediate product and most of it converts to CO_2 .

6.6 Effect of geometry

A sensitivity analysis is done here to investigate the effect of permeate channel height on the oxygen permeation rate and oxy-combustion characteristics considering the real ITM reactor application. All the parameters are fixed like the base case and only the permeate channel height is changed. Figures 6.10 and 6.11 are used to investigate this sensitivity analysis regarding reactor geometry with considering a real combustion model. As shown

in Fig.6.10, part (a), the oxygen permeation rate has a reverse behavior to the permeate channel geometry and it is reduced by increasing the channel height. This is due to the reduced effect of the flow momentum by increasing the channel height as the velocity of the flow will be reduced by increasing the area.

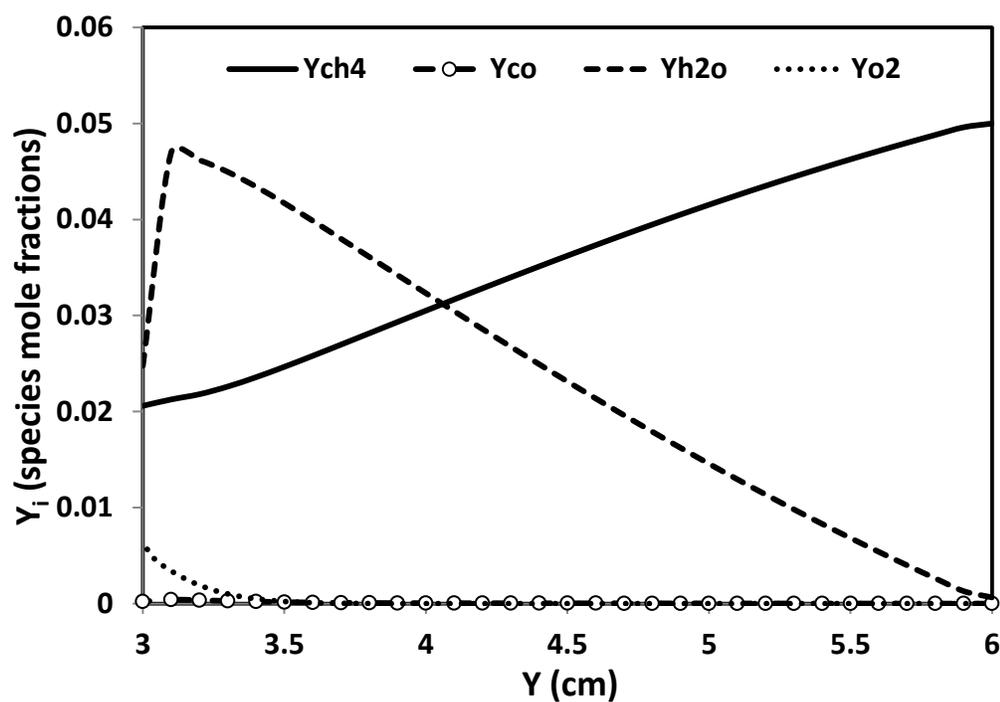


Figure 6.9 Species mole fractions distributions inside the reaction zone at 5/95% Vol. CH₄/CO₂, feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}^* = 0.21$ atm.

As a result of increased oxygen flux by reducing the channel height, the oxygen partial pressure inside the feed zone is reduced indicating higher oxygen flux and highlighting the effect of flow momentum inside the permeate zone on oxygen permeation rate as shown in Fig.6.11. However, the maximum temperature inside the reaction zone will be increased with the channel height indicating better mixing between the sweep reactants and the permeated oxygen due to reduced flow velocity. Also, the maximum temperature region starts to move little bit away from the membrane surface as the channel height is increased as shown in Fig.6.10, part (b) and as a result, the amount of heat absorbed by the membrane will be reduced.

Due to the lowered oxygen permeation flux as the channel height increase, the combustion zone shifts away from the membrane surface and hence more oxygen will be available near to the membrane surface and this may justify the higher oxygen partial pressure inside the permeate zone near to the membrane surface in case of increasing the permeate channel height as shown in Fig.6.11.

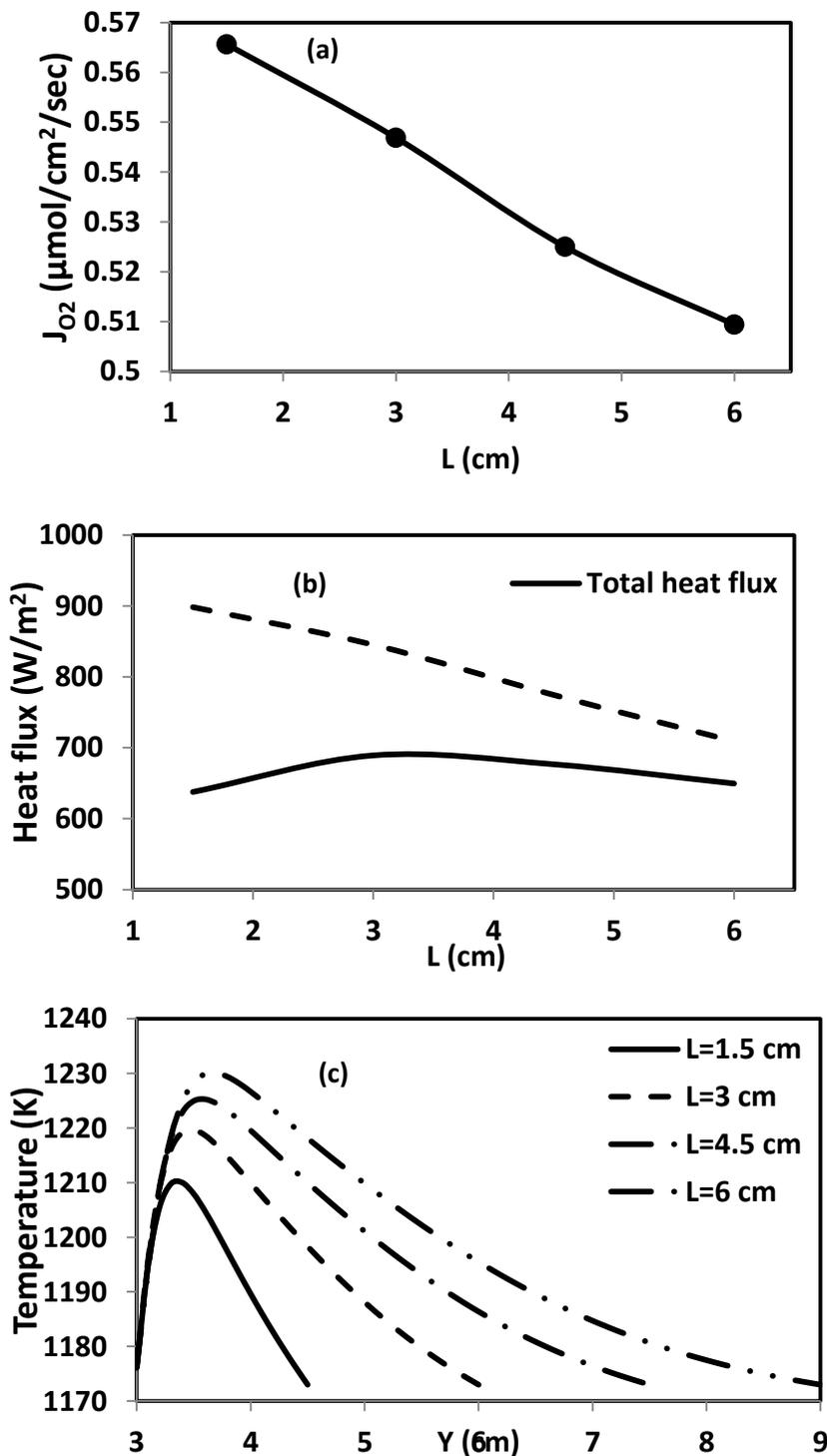


Figure 6.10 Influences of normal distance to the membrane, L , on: (a) oxygen permeation flux, (b) total heat flux through the membrane surface to the feed zone and absorbed radiation heat flux and (c) temperature distribution inside the reaction zone at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P_{O_2}=0.21$ atm.

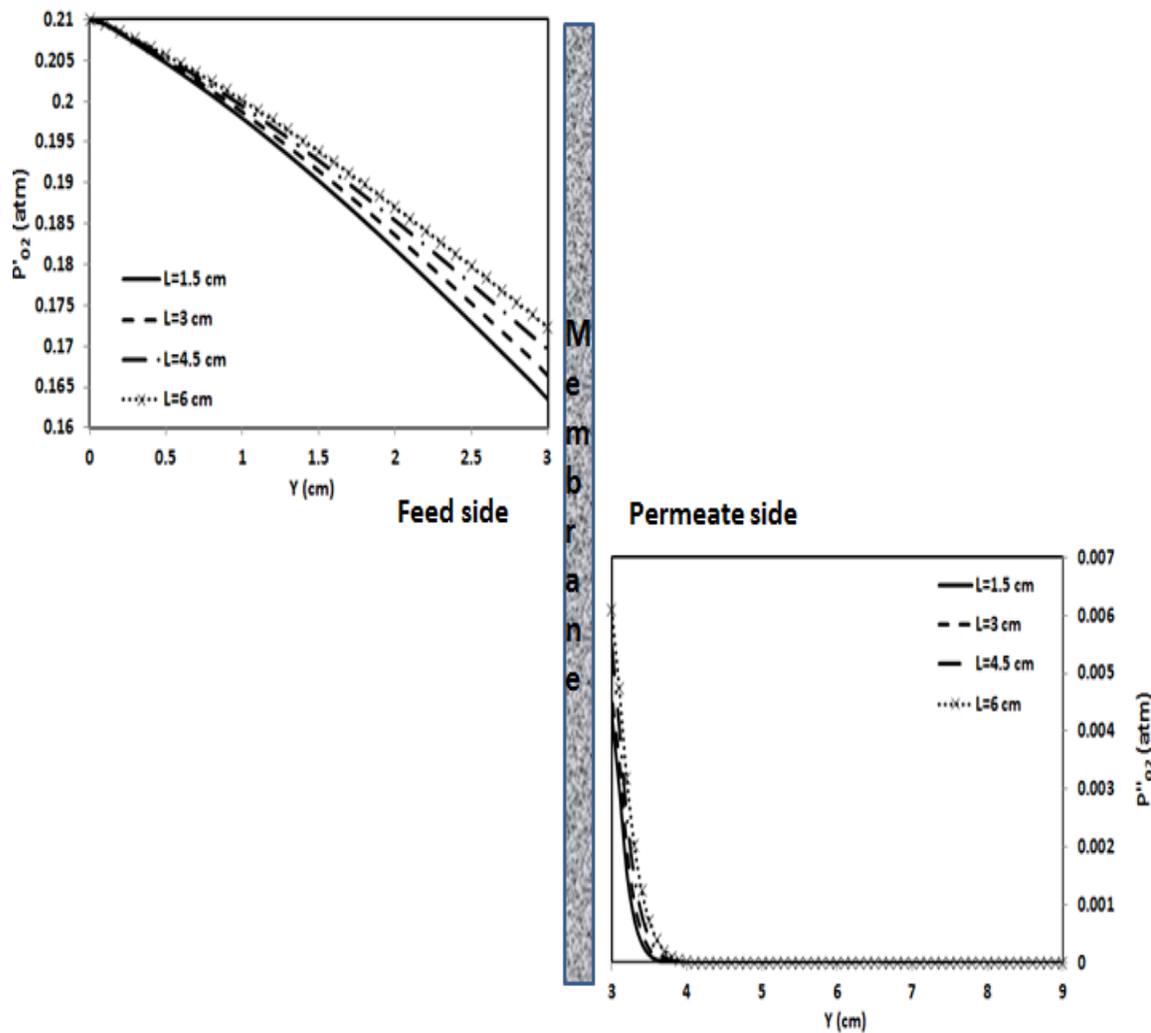


Figure 6.11 influences of normal distance to the membrane , L , on oxygen partial pressure distribution in both sides of the membrane at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P_{\text{O}_2}=0.21$ atm.

6.7 Influence of operating conditions

6.7.1 Effect of percentage of CH₄/CO₂ in the sweep gas mixture

As discussed above in the present work, as the percentage of CH₄ increases in the sweep gas as the oxygen permeation flux increases. However, in all cases, the amount of oxygen permeation is not enough for complete combustion of CH₄. As shown in Fig.6.12, part (a), the maximum temperature inside the reaction zone is increased as the percentage of CH₄ is reduced in the sweep gas mixture. This is due to improved ratio of the available permeated oxygen moles to the coming CH₄ moles in sweep gas. When this ratio is more close to the stoichiometric ratio, the combustion temperature will be increased however; the oxygen permeation flux is reduced as the percentage CH₄ in the sweep mixture is reduced. Also it is clear from the temperature plots that the combustion starts early away from the membrane surface and the maximum temperature region is moved away from the membrane surface when the percentage of CH₄ is decreased in the sweep gas mixture. There is no increase in the temperature in case of mixing operation (non-reacting) as shown in the figure. Part (b) of the same figure, Fig.6.12, shows the amount of radiant heat flux absorbed by the membrane surface and the total heat flux through the membrane surface. Part of the absorbed heat is moves through the membrane surface to the air side and the other part is kept by the membrane and this part of heat causes the increase in the membrane temperature. It is obvious also from the figure that as the CH₄ % increases in the sweep gas mixture as the amount of heat transfer through the membrane increases however the maximum temperature was decreased. This may because the maximum

temperature region moves away from the membrane surface when the CH_4 % is reduced in the sweep mixture.

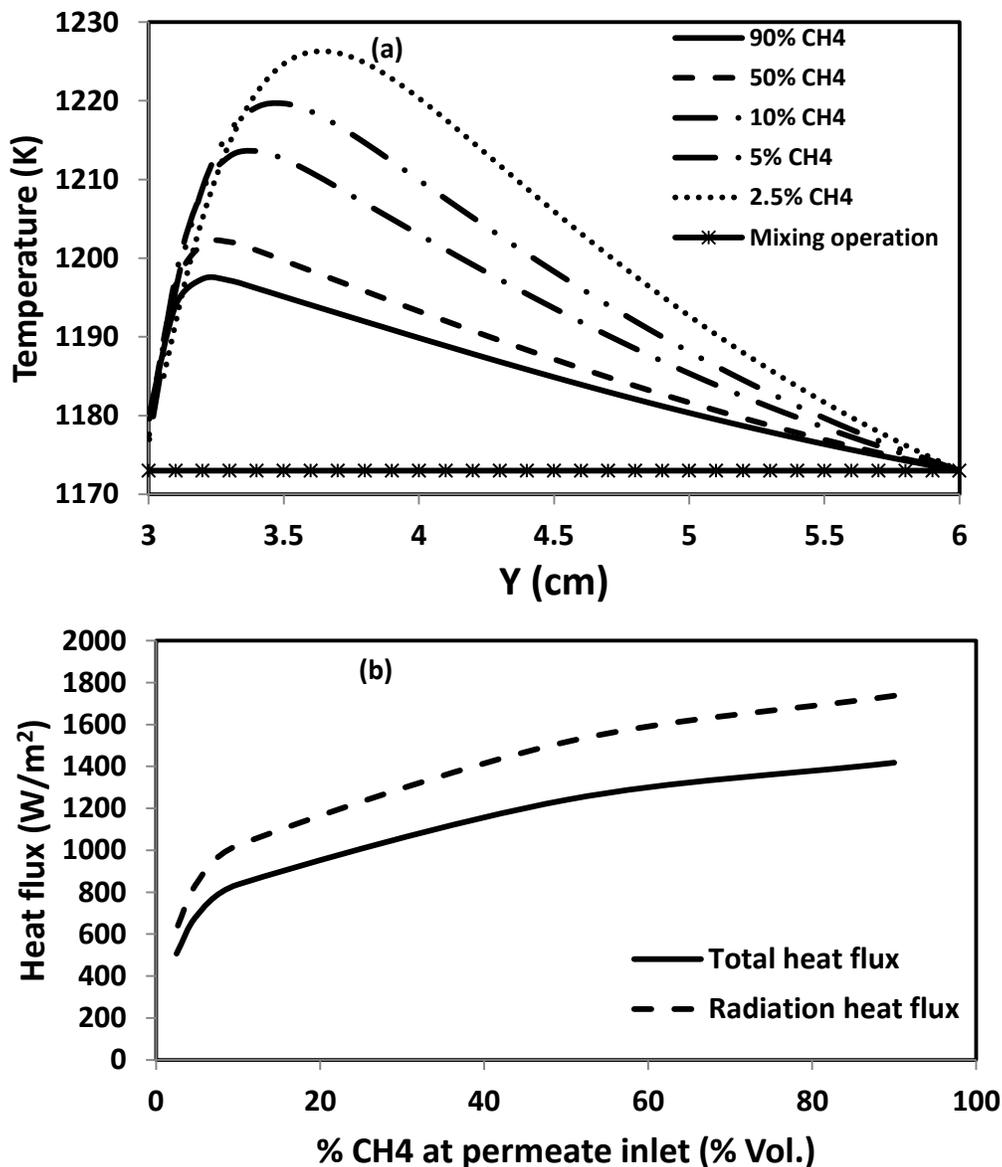


Figure 6.12 Influences of % CH_4 in the sweep gas mixture (CH_4+CO_2) on: (a) temperature distribution inside the reaction zone. (b) total heat flux through the membrane surface to the feed zone and absorbed radiation heat flux at feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{\text{O}_2}=0.21$ atm.

Also, due to the high reactor temperature as compared to the reactor geometry, the strain rate will be increased due to reduced density and so increased velocity. This high strain rate leads to squeezing of the flame into a small region and this will lead to higher maximum heat release rate in the reaction zone. The flame zone also is near to the membrane surface as shown above and this will lead to heating up of the membrane and reduced maximum temperature inside the reactor due to higher heat loss to the air side through the membrane surface. Figures 6.13 and 6.14 are showing the profiles regarding the reactions rates profiles and the mole fraction distribution for each reacting species. Figure 6.13, part (a), shows the rates of reaction 1 for different percentages of CH_4/CO_2 as sweep gases. As discussed above, the oxygen permeation rate and hence the oxygen concentration on the permeate side are rather low, resulting in a fuel-rich environment in the reaction zone. In this case, instead of being fully converted to carbon dioxide (complete combustion), methane is partially oxidized to form carbon monoxide and water vapor, as introduced in table.3.2 for the first reaction. Then, the carbon monoxide comes out from the first reaction react with oxygen and produce carbon dioxide which is reaction 2. The amount of oxygen permeation flux was increased when the CH_4 % was increased in the mixture and as a result the reaction 1 rate will be increased and as a result also reaction rate 2 will be increased according to the availability of oxygen as shown in Fig.6.14. As we can see from Fig.6.14, part (b), when the CH_4 % is increased, the amount of CO is increased and because of increased oxygen permeation flux, the reaction rate of reaction number 2 was increased. Also, from both figures, figures 6.13 and 6.14, the reaction rates for both reactions are almost zero in most of the reactor except in the region near to the membrane indicating lack of oxygen in those regions.

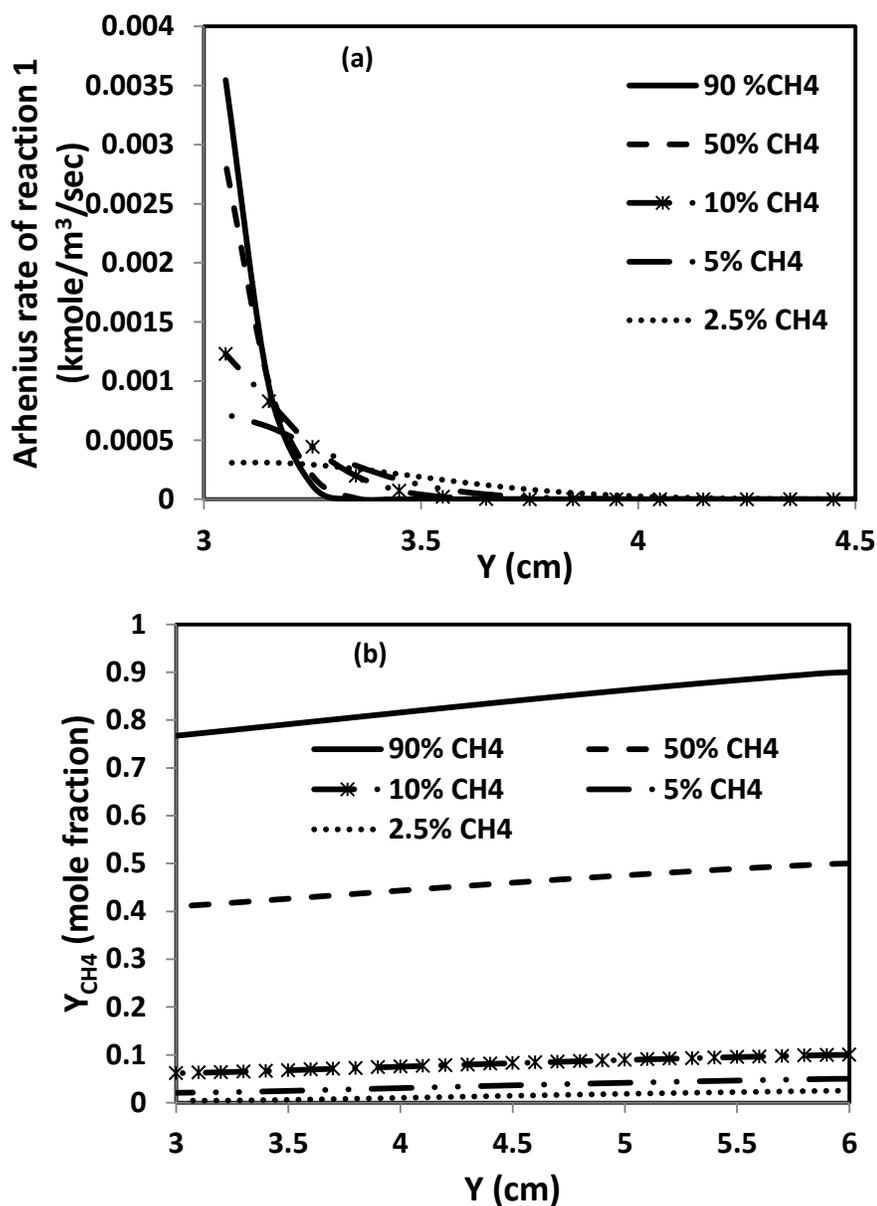


Figure 6.13 Influences of %CH₄ in the sweep gas mixture (CH₄+CO₂) on: (a) rate of reaction 1. (b) mole fractions distribution of CH₄ at feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and P_{O₂}'=0.21 atm.

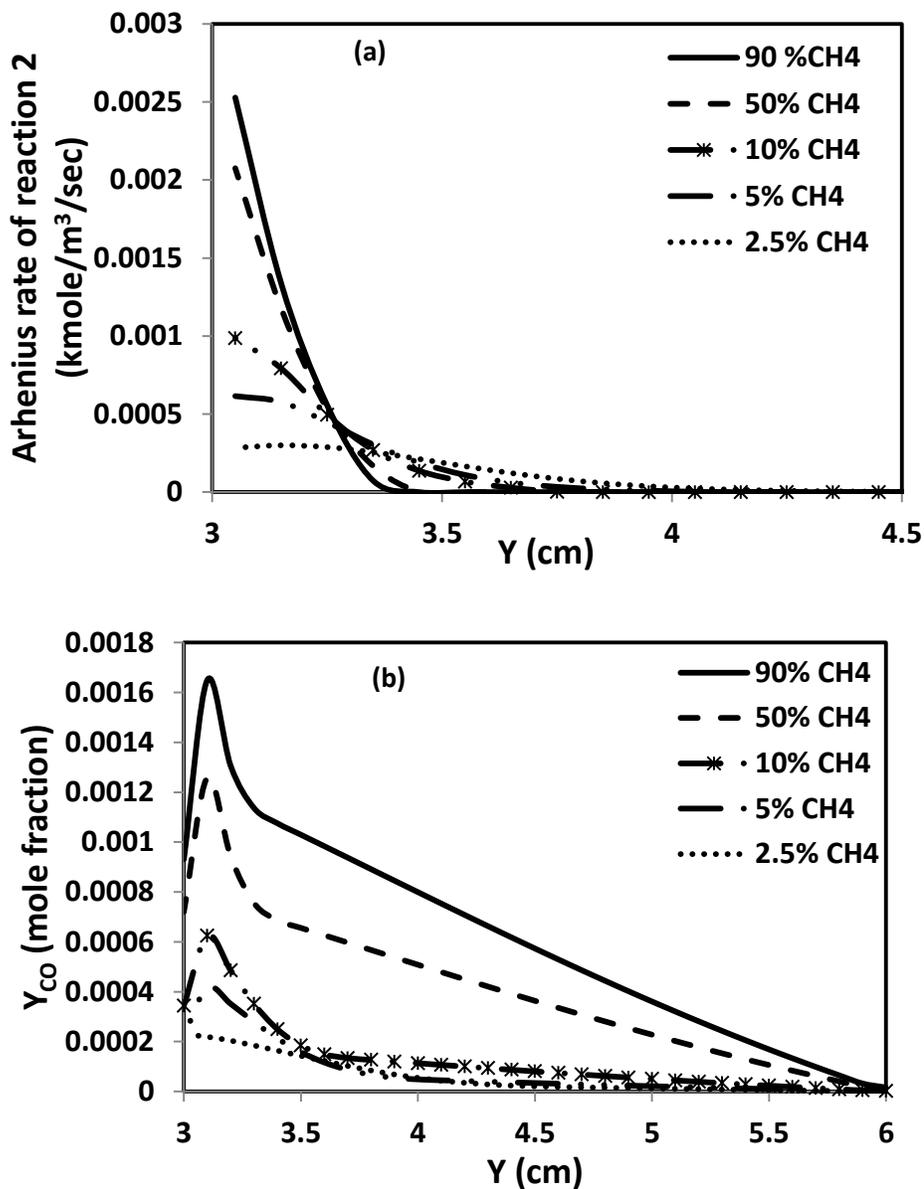


Figure 6.14 Influences of %CH₄ in the sweep gas mixture (CH₄+CO₂) on: (a) rate of reaction 2. (b) mole fractions distribution of CO at feed and sweep gases volume flow rate and inlet temperature of 500 sccm and 1173 K respectively and $P_{O_2}=0.21$ atm.

6.7.2 Effect of inlet gases temperature (feed and sweep)

The inlet temperature of gases in both sides of the membrane is a very important parameter regarding the oxygen permeation flux. From oxygen permeation equation, the oxygen flux is directly dependent on membrane temperature and as the temperature increases as the oxygen flux increases because of the reduction in the surface exchange resistance of the membrane. Figure 6.15, part (a), confirms this way of dependence of oxygen permeation on the inlet gases temperature in case of reactions are activated in the permeate side of the membrane. If those values of oxygen permeation flux (see Fig.6.15, a) are compared to the inert operation (argon is used as sweep gas) for the same feed and sweep volume flow rates, one can found that the values of the oxygen permeation flux are increased to roughly three times more because of reactions activation in the permeate side and the effective permeation process when CO_2 and CH_4 are used as sweep gases as compared to argon.

As the inlet gases temperature increases as the oxygen permeation flux increases and so more complete combustion will be encountered and the maximum temperature inside the reactor will be increased as shown in Fig.6.15, part (c) causing more radiant heat to be absorbed by the membrane surface and more heat flux to the feed side domain as shown in the same figure, part (b). The partial pressure of oxygen in feed zone, P_{O_2} , was found to be reduced when the inlet gas temperature was increased indicating more oxygen permeation flux. In the permeate side, for the case of inlet temperature of 973 K, the oxygen permeation flux is very small as compared to the other cases and as a result, the reactions will proceed very slowly and the increase in temperature is negligible.

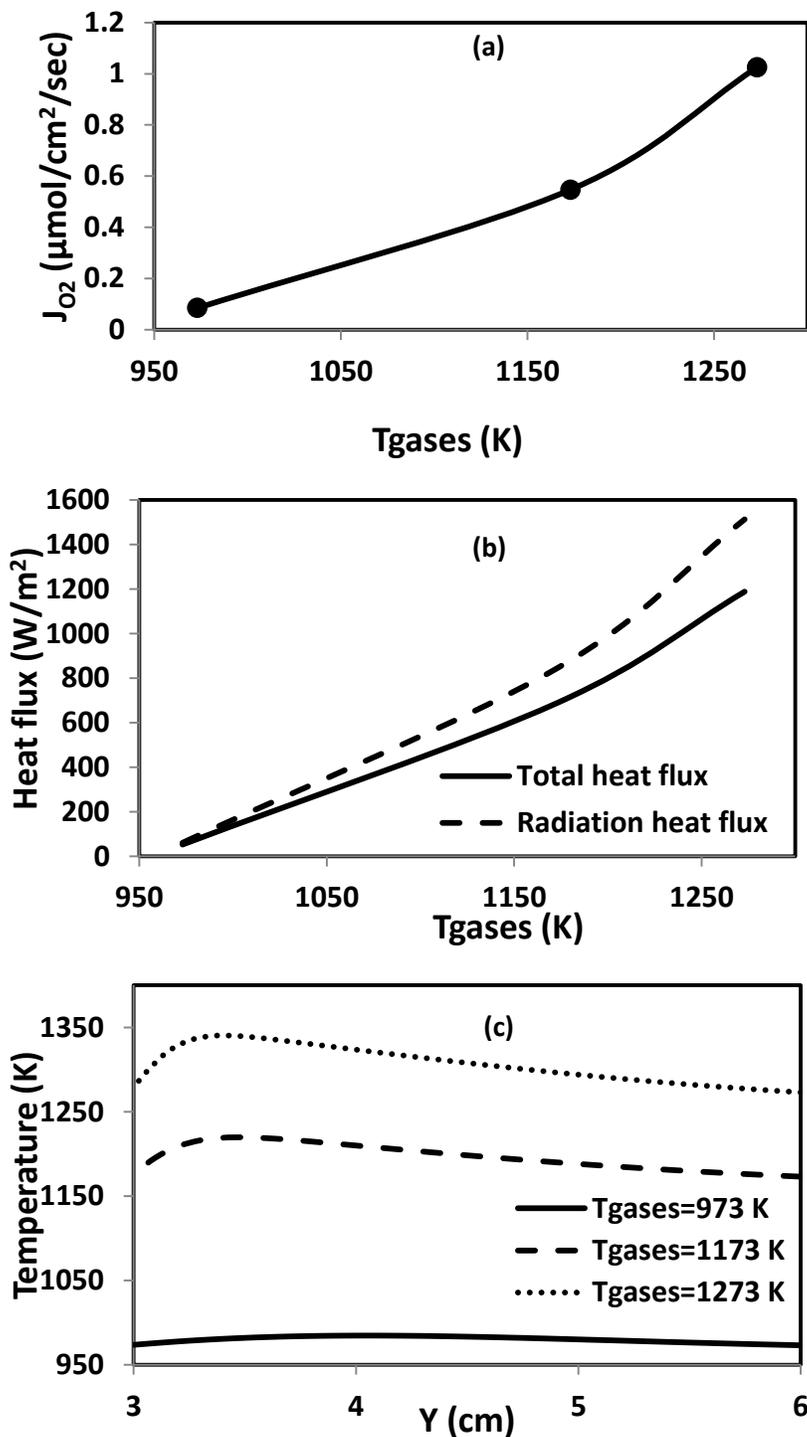


Figure 6.15 Influences of feed and sweep gases inlet temperature on: (a) oxygen permeation flux, (b) total heat flux through the membrane surface to the feed zone and absorbed radiation heat flux and (c) temperature distribution inside the reaction zone at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P_{\text{O}_2}=0.21$ atm.

So, oxygen molecules were found to be available everywhere inside the permeate zone because of very weak combustion in this case. For the other high inlet gas temperature cases, only oxygen is available near to the membrane surface and then it is completely consumed in the combustion process as the combustion is much more effective in those cases.

To see more about the oxygen permeation, Figure 6.16 shows the partial pressure distribution of oxygen in both sides of the membrane. As shown, the partial pressure of oxygen in feed zone, P_{O_2} , is reduced as the inlet gases temperature increase indicating more oxygen permeation flux as explained above. In the permeate side, for the case of inlet temperature of 973 K, the oxygen permeation flux is very small as compared to the other cases and as a result, the reactions will proceed very slowly and the increase in temperature is negligible. So, we can see oxygen molecules are available everywhere inside the permeate zone because of very weak combustion as shown in Fig.6.16. As compared to the other cases, only oxygen is available near to the membrane surface and then it is completely consumed in the combustion process as the combustion is much more effective in those cases.

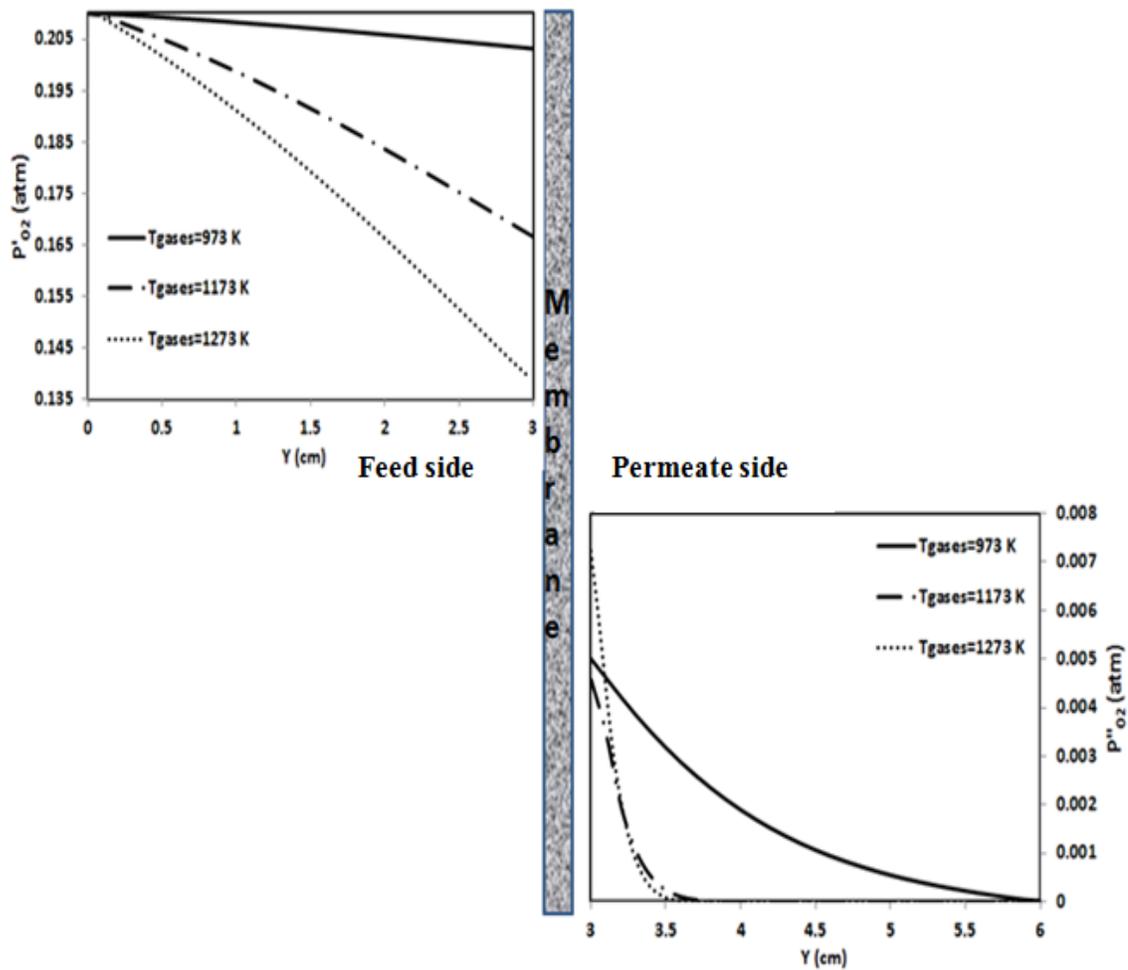


Figure 6.16 Influences of feed and sweep gases inlet temperature on oxygen partial pressure distribution in both sides of the membrane at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P'_{O_2}=0.21 \text{ atm}$.

6.7.3 Effect of oxygen partial pressure in feed side (P'_{O_2})

In this section, a sensitivity analysis regarding the feed side oxygen partial pressure is introduced. Figure 6.17 explains the effect of feed side oxygen partial pressure on both the oxygen permeation flux and oxy-combustion process for the same sweep and feed flow rates. As shown in the graph, part (a), the amount of oxygen permeation flux increases as the oxygen partial pressure in the feed side increases. The reason is that the oxygen permeation flux is dominated by the difference in oxygen partial pressure across the membrane and the membrane temperature, as it is clearly shown in the permeation flux equation. Then, the changes in the P'_{O_2} will affect the oxygen permeation directly, as shown in Fig.6.17, part (a). However, the increase in the oxygen flux is very small and this fact is indicating the main dependence of oxygen permeation flux on the temperature rather than the oxygen partial pressure and the temperature difference is small as shown in Fig.6.17, part (c) then, the differences in oxygen permeation rate is small.

The greater the P'_{O_2} , the larger the driving force for oxygen permeation. Also, as a result of increased oxygen flux, the combustion process is improved slightly and the maximum temperature inside the reaction zone is increased a little bit as shown in Fig.6.17, part (c). The amount of heat transfer absorbed and across the membrane is also increased slightly by increasing the oxygen partial pressure in the feed side (see Fig.6.15, part (b)). The values of the oxygen partial pressure in the permeate side are increased very slightly near to the membrane surface due to the slightly improved oxygen flux. Figure 6.18 shows also the partial pressure distribution of oxygen as a function of feed side oxygen partial pressure at feed inlet. The values in the permeate side are increased very slightly near to the membrane surface due to the slightly improved oxygen flux.

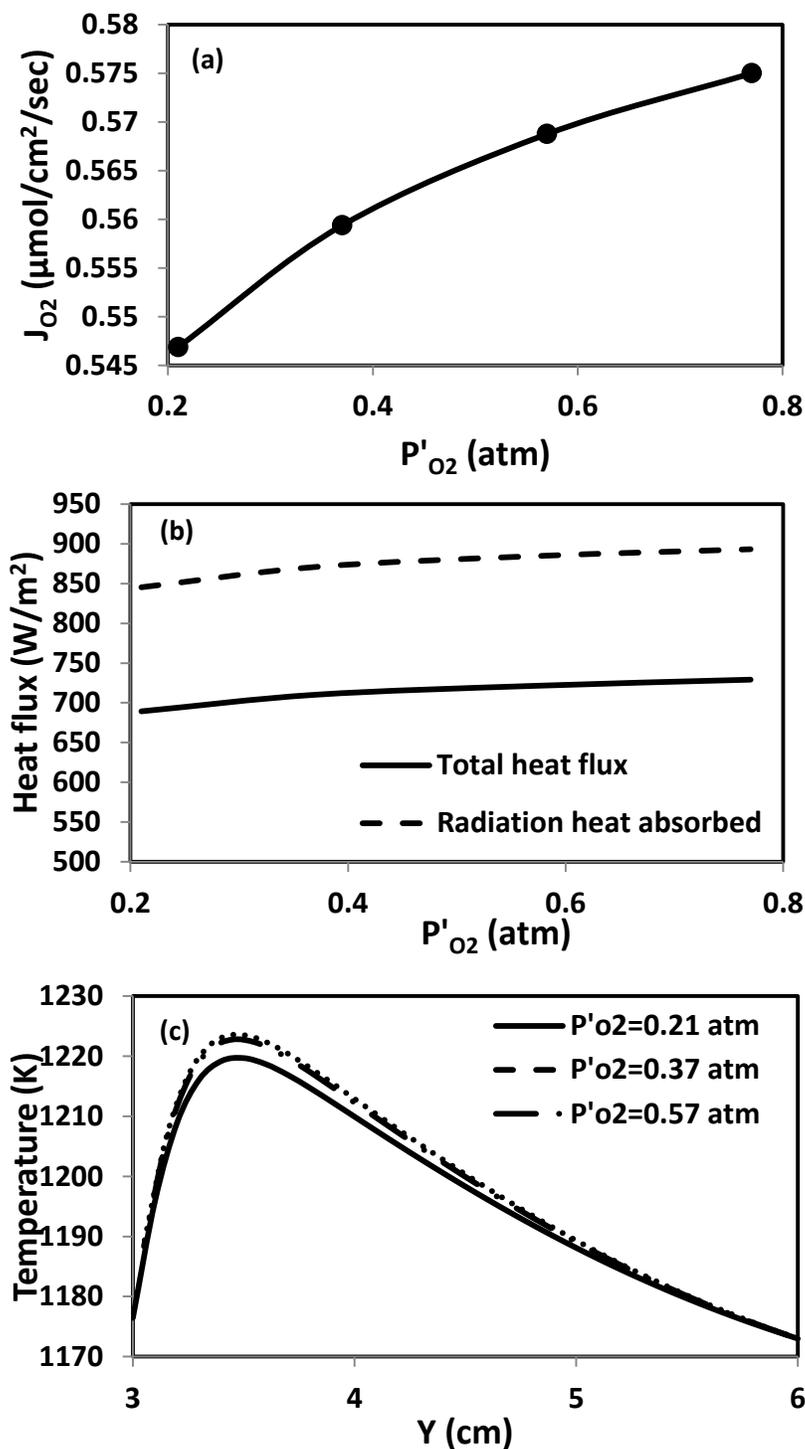


Figure 6.17 Influences of partial pressure of O_2 , P'_{O_2} , on: (a) oxygen permeation flux, (b) total heat flux through the membrane surface to the feed zone and absorbed radiation heat flux and (c) temperature distribution inside the reaction zone at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P'_{O_2}=0.21$ atm.

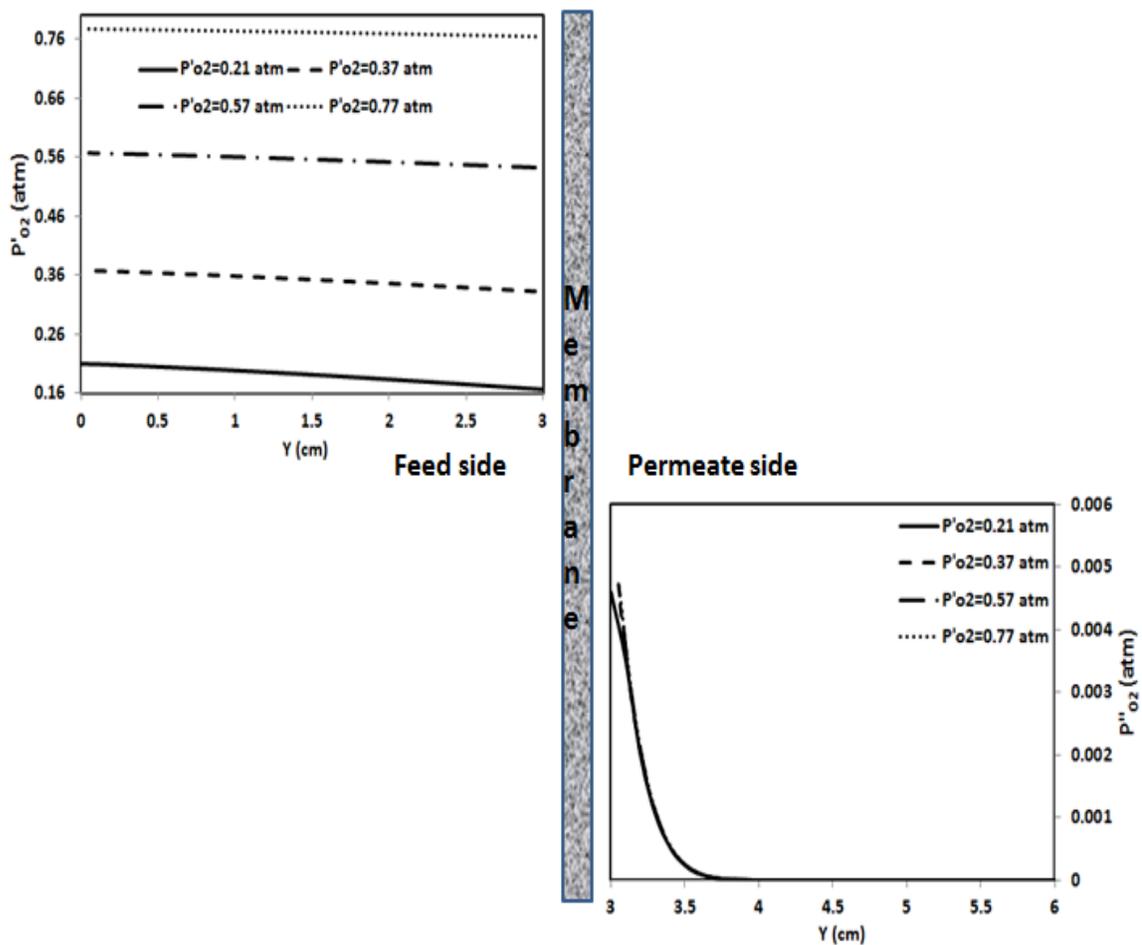


Figure 6.18 Influences of partial pressure of O_2 , P'_{O_2} , on oxygen partial pressure distribution in both sides of the membrane at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P'_{O_2}=0.21$ atm.

6.7.4 Effect of sweep gases flow rate

The sweep gases mass flux has an enhancing effect on the oxygen permeation flux. However, the change in oxygen permeation flux is slight as shown in Fig.6.19, part (a) due to the main dependence of oxygen permeation on the membrane temperature rather than the oxygen partial pressure in both sides of the membrane as in all cases in Fig.6.19, the combustion process is activated and as a result the membrane temperature was increased. The increase in the sweep gases mass flux results in increase in the oxygen permeation flux due to the reduction in the oxygen partial pressure in the permeate side. Furthermore, the permeate side oxygen partial pressure does not change much with the sweep volume flow rate and as a result the amount of oxygen permeation will not be affected that much and after certain volume flow rate, no increase in the oxygen permeation flux will be encountered as shown in Fig.6.19, part (a). Due to the slight increase in the oxygen flux as a function of sweep gases volume flow rate, the combustion temperature was increased by a small number of degrees as shown in Fig.6.19, part (c) and there is also a slight improvement in the amount of heat flux through the membrane as shown in the same figure, part (b). In the above analyzed part of the present study, a modified two step finite rate reaction kinetics model for methane oxy-combustion has been introduced in order to predict the oxy-fuel combustion characteristics inside an ITM reactor. A detailed 2D study has been presented herein the present work to understand more the performance of an ITM reactor under the oxy-combustion conditions in the permeate side of the membrane. Also, Coefficients of the oxygen permeation equation have been introduced for a LSCF1991 ion transport

membrane based on the fitting of the experimental data in the literature. The analysis of the effect of reactivity on the permeation process has been discussed.

The effects of many parameters including inlet gases temperature (feed and sweep), reactor geometry, feed and sweep volume flow rates, oxygen partial pressure in the feed side and the effect of the percentage of CH_4 in the sweep gases mixture on the permeation process and oxy-combustion characteristics have been analyzed. From the sensitivity analysis done above, we can say that there are important parameters affecting the operation of ITM reactors (reactions are activated) like the inlet gases temperature (feed and sweep), percentage of CH_4 in the sweep gases mixture and the reactor geometry. Also, there are less important parameters like, feed and sweep volume flow rates, oxygen partial pressure in the feed side. From the above analysis, we can conclude that the chemical reactions have a great effect on enhancing the oxygen permeation flux.

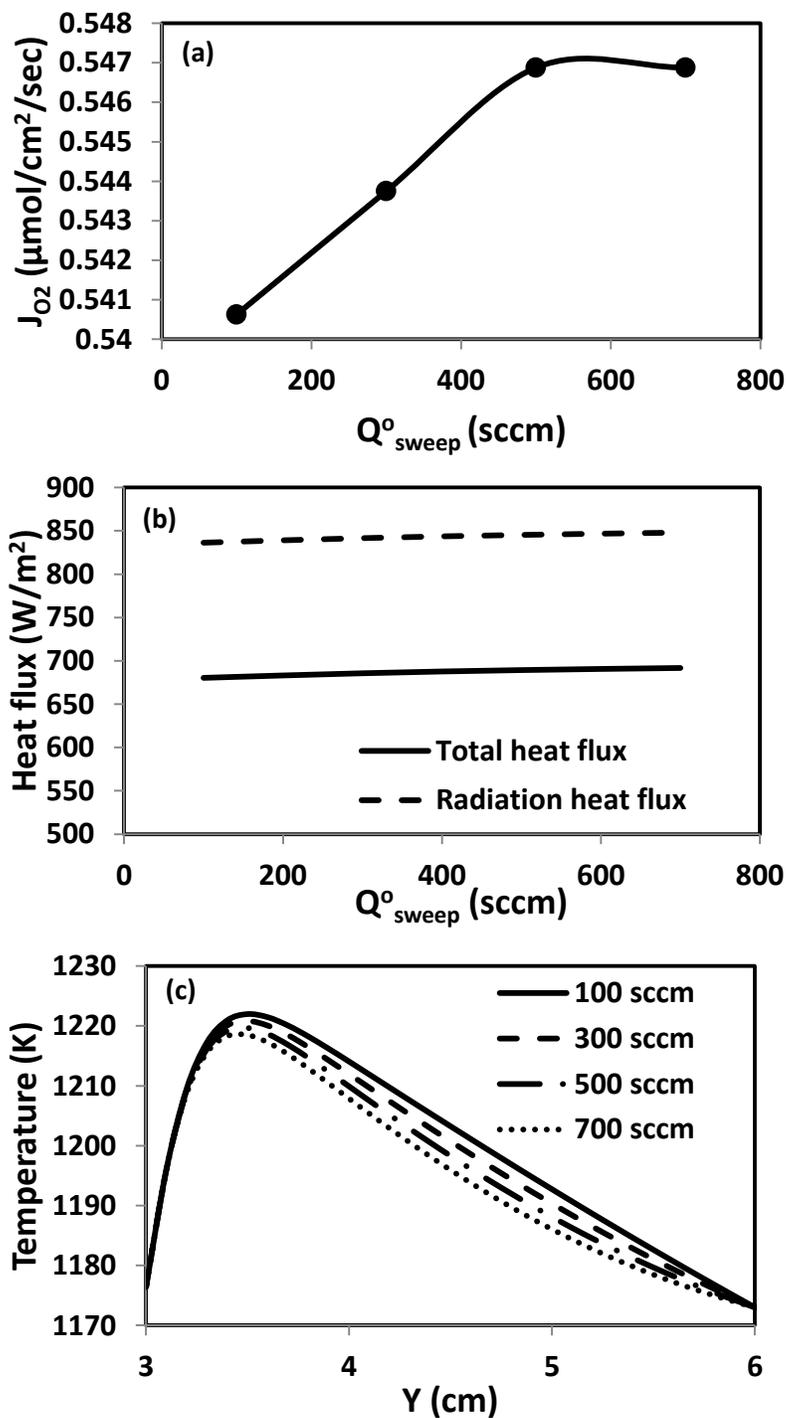


Figure 6.19 Influences of sweep gases volume flow rate on: (a) oxygen permeation flux, (b) total heat flux through the membrane surface to the feed zone and absorbed radiation heat flux and (c) temperature distribution inside the reaction zone at feed and sweep gases volume flow rate of 500 sccm, 5/95% Vol. CH_4/CO_2 and $P_{\text{O}_2}=0.21$ atm.

CHAPTER 7

RESULTS AND DISCUSSIONS OF THE 3D SIMULATIONS FOR THE SUBSTITUTION OF ITM REACTOR INTO GAS TURBINE COMBUSTOR

Little work was reported with a focus on examining the effects of reaction side conditions and flow configuration on oxygen permeation through the mixed-conducting ceramic membranes and none has been performed for 3-D membrane reactors. In the present study, focus is made on oxygen separation through ion transport membranes and then the combustion is made in the permeate channels with fuel in a mixture of $O_2/CO_2/H_2O$. The new reactor design introduced here is substituting conventional gas turbine combustor by a monolith structure ITM reactor. Optimization for the feed and sweep flow rates have been done in order to meet the power required for the reactor and keeping the reactor size as compact as possible. Effects of flow configurations, channel width and percentage of CH_4 in the permeate side flow are also introduced under constant inlet gas temperature and fixed operating pressure of 10 bars. The reactor geometry has been optimized based on the optimization of channel width. Accordingly, the number of permeate and feed channels has been calculated keeping the reactor size as close as possible to the size of a real industrial gas turbine. The monolith structure reactor design introduced here is able to give power ranging from 5 to 8 MWe based on cycle first law efficiency.

The present work is aiming to introduce an ITM reactor design that is able to substitute a gas turbine combustor. To produce such design, optimizations are required for many parameters affecting the reactor performance specially the amount of volume flow rates in feed and permeate sides, channel width and the percentage of CH₄ in the permeate side flow. The permeate stream has an upper-bound on diluent flow-rate because the inlet methane concentration should not fall below roughly 5% for mass transfer and combustion stability reasons. For this reason, the percentage of CH₄ in the permeate channels was kept at 5% Vol. and the flow rates in both sides of the membrane were changed in order to get maximum oxygen permeation flux and complete conversion of CH₄ in the permeate channels.

It was found from the simulations that any reduction in the channel width below 15 mm results in large increases in the viscous pressure drop. Basically, as the channel width decreases, the flow velocity must increase to maintain the same mass flow-rate. The combustion also due to this high flow velocity was lost. The channel length was considered fixed in all simulations to 0.9 m to be similar to the operating length of a real gas turbine combustor and the operating pressure for both streams was fixed to 10 bars. The total number of channels was calculated in order to get as compact design as possible for the ITM reactor and give a reasonable operating power output. A monolith structure design ITM reactor is used here in the present study with total number of feed and permeate channels of 50,000, 25,000 for each stream. The membranes separate oxygen containing streams (typically air) from streams containing the fuel, methane, and the sweep gas, CO₂ plus H₂O. The present reactor design results in reactor height of 3.35 m

and overall volume and membrane surface area of 10 m^3 and 2700 m^2 , respectively. The reactor is able to deliver power ranging from 5 to 8 MWe based on cycle first law efficiency. In order to understand how an ITM reactor depends on the flow configuration, calculations are performed for co-current versus counter current at the same operating conditions. The ITM reactor specifications for the substituting a gas turbine combustor are listed in table 7.1.

TABLE 7.1 Membrane reactor specifications for substituting a gas turbine combustor

parameter	Reactive co and counter-current
Permeate T_{in} [K]	1173
Feed T_{in} [K]	1173
Feed $m \bullet_{air}$, [kg/s/cell]	$1.4336 \cdot 10^{-3}$
Permeate $m \bullet_{CH_4}$, [kg/s/cell]	$1.54944 \cdot 10^{-5}$
5 % Vol.	
Permeate $m \bullet_{CO_2, in}$ [kg/s/cell]	$4.289 \cdot 10^{-4}$
Permeate $m \bullet_{H_2O, in}$ [kg/s/cell]	$1.754 \cdot 10^{-4}$
Feed P_{tot} [bar]	10
Permeate P_{tot} [bar]	10
Number of cells per stream	25,000
Power [MW], bases on 1 st law efficiency.	5:8

7.1 Model validation

Figure 7.1 compares the present model calculation results with the work done by Mancini and Mitsos [164]. For this validation case, the counter current flow configuration cases considered in their work was conducted using our present model and the data for oxygen permeation flux and oxygen partial pressure in both sides of the membrane were compared as shown in the figure. Due to the reactor symmetry, only four adjacent quarters of four adjacent cells are considered in this simulation. The calculations were performed at fixed pressure of 10 bars in both sides of each membrane and feed and permeate inlet temperatures of 973 K and 1173 K, respectively. The total flow rates of feed gases for all reactor cells (100,000 cells, 50,000 cells per stream) are O_2 (3.3 kmol/s), N_2 (12.41 kmol/s) and H_2O (1 kmol/s). Also, the total permeate gases flow rates for all reactor cells are CO_2 (8.34 kmol/s) and H_2O (8.34 kmol/s).

One can see that the oxygen permeation flux profiles for the present calculations and the reference work calculations are in a good agreement and the flux drop from inlet to exit direction. This flux drop is due to the increased oxygen partial pressure in the permeate side of the membrane as shown in the same figure, lower plot. Also, the oxygen mole fraction of the feed stream drops sharply in the case of counter current configuration indicating a high recovery ratio, and an effective ITM configuration as shown in Fig.7.1.

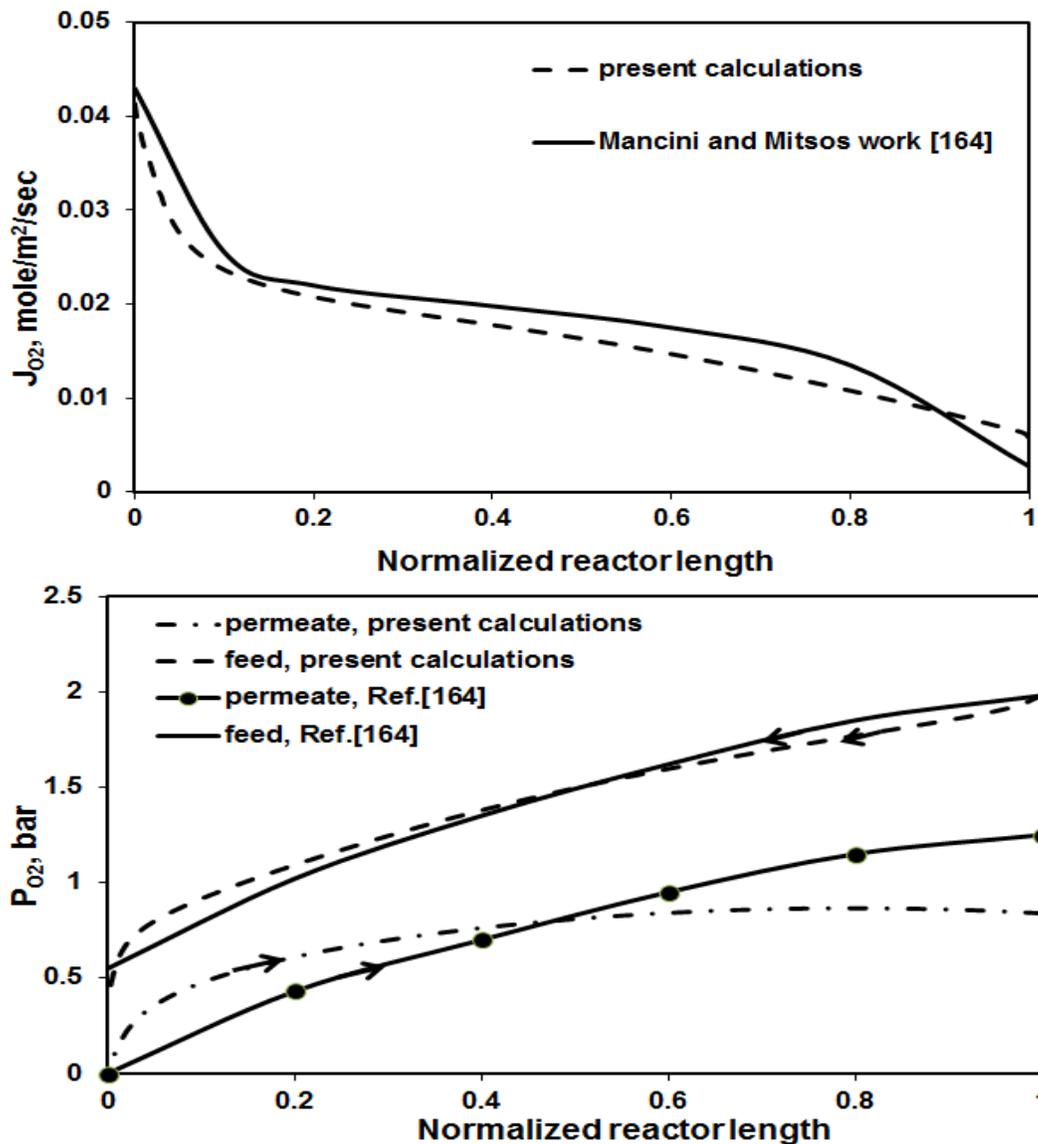


Figure 7.1 Counter-current separation-only: axial dependence of oxygen permeation flux and oxygen partial pressure at fixed pressure of 10 bars in both sides of the membrane for the present calculations and the work done by Mancini and Mitsos [164].

7.2 Co-current reactor design

Most of the analysis in the present work is related to the co-current flow configuration because of membrane temperature rise problems. In case of counter-current flow, the membrane temperature is increased exceeding the permissible operating range of the membrane as it is discussed in the coming section. The counter-current has the lowest average partial pressure driving force, but an analogy to heat exchangers explains this apparent contradiction as the counter current heat exchangers has higher efficiency than the co-current exchangers. The overall mass transfer coefficient depends on both the average wall temperature and average partial pressure driving force. Thus, since the average wall temperature is higher, the average partial pressure driving force must be higher if the same operating conditions are applied.

The combustion starts close to the membrane surface at axial location close to 0.15 m and due to the sudden increase in temperature at this region, a jump in oxygen permeation flux occurs at this region as shown in Fig.7.4. The permeate gas temperature rises slowly at first due to slow oxygen transport starting from 1173 K at inlet and then increases gradually to reach 1400 K at exit plane. To see the flame zone shape and its size development on the axial direction, Fig.7.2 is showing the temperature contour plots at different axial locations on planes normal to the flow direction. The flame starts in a small region in the corners between membranes in the permeate channels. The size of the flame starts to increase in the axial direction till it fills the whole permeate channels at axial location of 0.8 m, close to the reactor exit plane, as shown in the figure.

Figure 7.3 shows the axial average temperature distribution of feed gas, membrane and permeate gas in part (a) and the axial average species mole fractions in the permeate side of the membrane in part (b). As shown in the figure, part (a), the membrane temperature rises slowly at the first part of the reactor due to slow oxygen transport and the resulting gradual combustion of the fuel. The permeate stream remains relatively close to the membrane temperature in this region because the convective heat transfer coefficient is high enough to accommodate the local heat release without a noticeable temperature difference. Due to the higher air flow rates and thus heat capacity in the feed channels, the average temperature of the feed flow remains low and little bit away from the membrane temperature. This increase in air flow rates has double merits enhancing the reactor operation, one is to cool down the membrane surface temperature because the combustion zone is very close to the membrane and the second is to increase the oxygen permeation flux [169,170].

The membrane temperature begins to increase faster than those of permeate and feed streams as the Arrhenius term in the flux constitutive relation increases rapidly, and the chemical reactions accelerate and the fuel is rapidly consumed. The implications of these results are that the local heat transfer coefficient is quite important because it dictates how much additional diluent is required, or equivalently, how much smaller the reactor channels must be to accommodate the localized excessive temperature. That is, unless local cooling can be provided precisely at the location where the membrane temperature overshoots, the heat transfer coefficient must be increased. That is, if only the transverse heat convection is sufficient to maintain the wall temperature within limits, then the

reactor is likely to meet this criterion easily when the effects of transverse radiative heat transfer are present and the application of ITM reactors into gas turbines is possible.

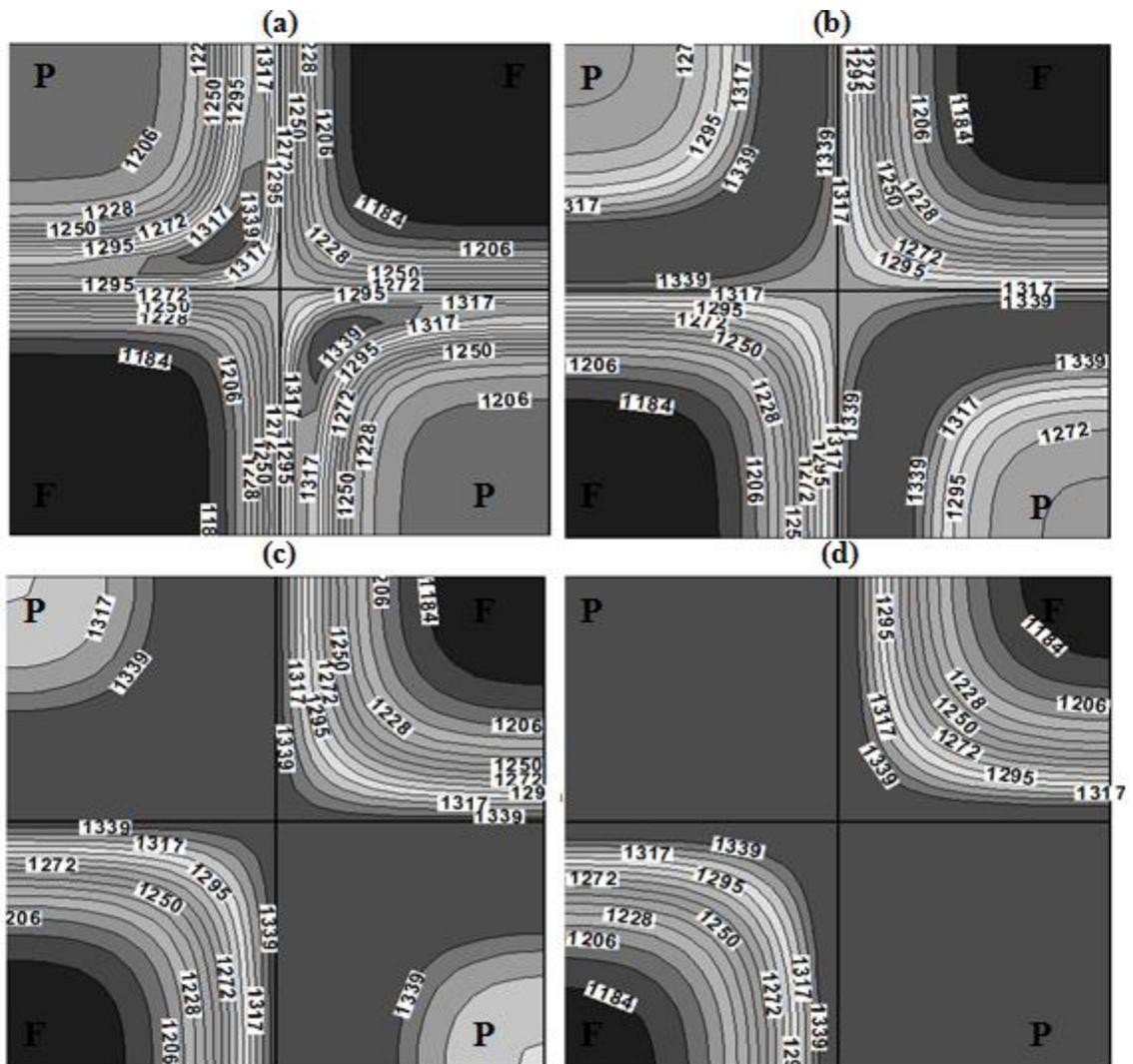


Figure 7.2 Co-current temperature contour plots at different axial locations through the reactor. a) $Z=0.2$ m, b) $Z=0.4$ m, c) $Z=0.6$ m and d) $Z=0.8$ m.

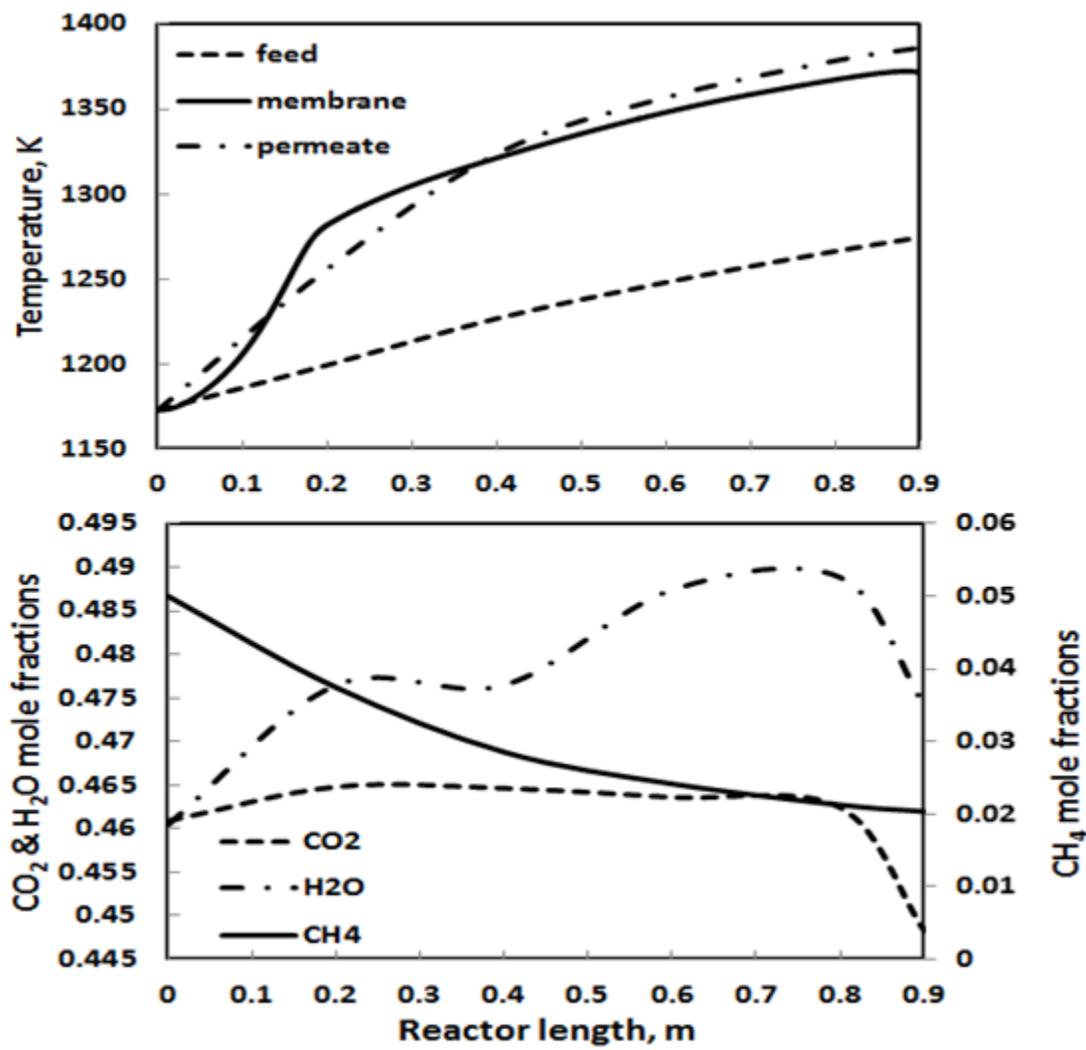


Figure 7.3 Co-current: a) axial average temperature distribution of feed gas, membrane and permeate gas and b) axial average species mole fractions in the permeate side of the membrane.

The average axial species mole fractions distributions are shown in Fig.7.3, part (b). The figure shows that the fuel starts to be consumed gradually from inlet to exit and the combustion is uniformly distributed through the reactor length. The reactions kinetics are sufficiently fast and that's why no fuel is present in significant amounts at reactor exit. The amount of CH_4 at exit section is around 2% of the total gases including the excess permeated oxygen and the whole combustion products of H_2O and CO_2 in addition to the inlet gases. The concentrations of H_2O and CO_2 are increased through the reactor length due to combustion as both of them are combustion products. However, their mole fractions are reduced at reactor exit section due to the reduction in the reaction rates and also due to the permeation of oxygen that is not consumed close to the reactor exit plane.

The longitudinal distributions of the average oxygen permeation flux and average local oxygen partial pressure in both sides of the membrane are shown in Fig.7.4. The results indicate that the flux drops significantly as the partial pressure of oxygen on the permeate side increases. This is due to higher sensitivity to the permeate partial pressures at large ratios of feed to permeate partial pressures. A jump in oxygen permeation flux occurs at axial distance of 0.15 m at which the combustion starts and the membrane temperature starts to increase sharply at this point. This behavior is a direct consequence of a dominant oxygen flux dependence on temperature than on partial pressure differences, and has serious implications for the feasibility of a reactive ITM. The increase in membrane temperature reduces the surface resistance of the membrane to oxygen permeation [190].

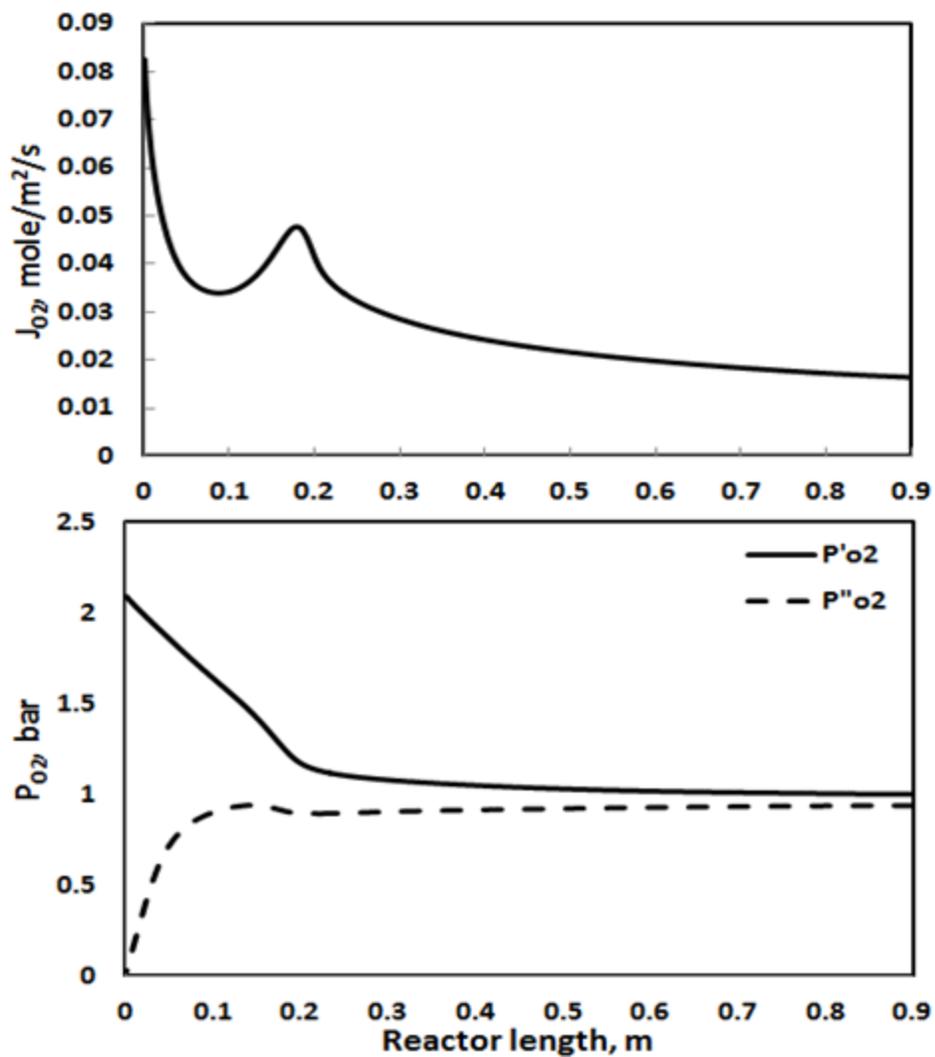


Figure 7.4 Co-current: a) axial oxygen permeation flux distribution and b) axial local oxygen partial pressure distribution in both sides of the membrane.

Further, the sudden acceleration of the oxygen flux as the temperature increases in a region of high partial pressure difference is the primary cause of the temperature overshoot, and could also have implications for materials stability. The increase in the oxygen partial pressure through the axial direction is due to the increased mass fractions of O_2 in the axial direction which can be seen easily in Fig.7.5 at different axial locations on planes normal to the flow direction.

As shown in the figure, the amount of O_2 increase in the axial direction in the permeate side and occupy larger area and it is reduced in the feed side. To capture a complete 3D view about the other parameters, Fig.7.6 is showing the contour plots of CH_4 , H_2O , CO_2 mole fractions distributions and axial velocity distribution, respectively, on a plane normal to the flow direction at axial location of $z=0.6$ m. in the permeate channels, the species concentrations are reduced close to the membrane surface due to oxygen permeation and the velocity is increased in the direction from the membrane surface to the channel centerline as shown in the figure.

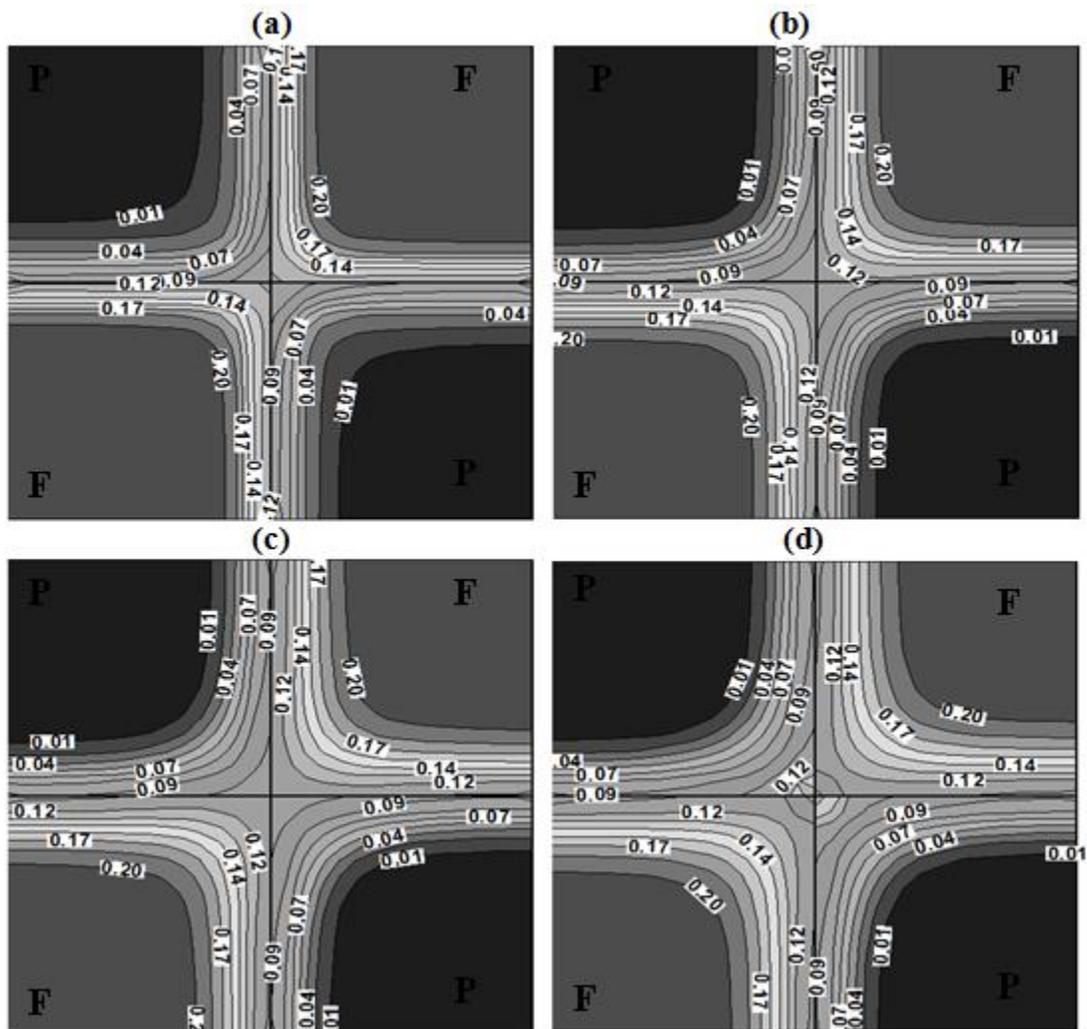


Figure 7.5 Co-current Oxygen mole fraction distribution at different axial locations through the reactor. a) $Z=0.2$ m, b) $Z=0.4$ m, c) $Z=0.6$ m and d) $Z=0.8$ m.

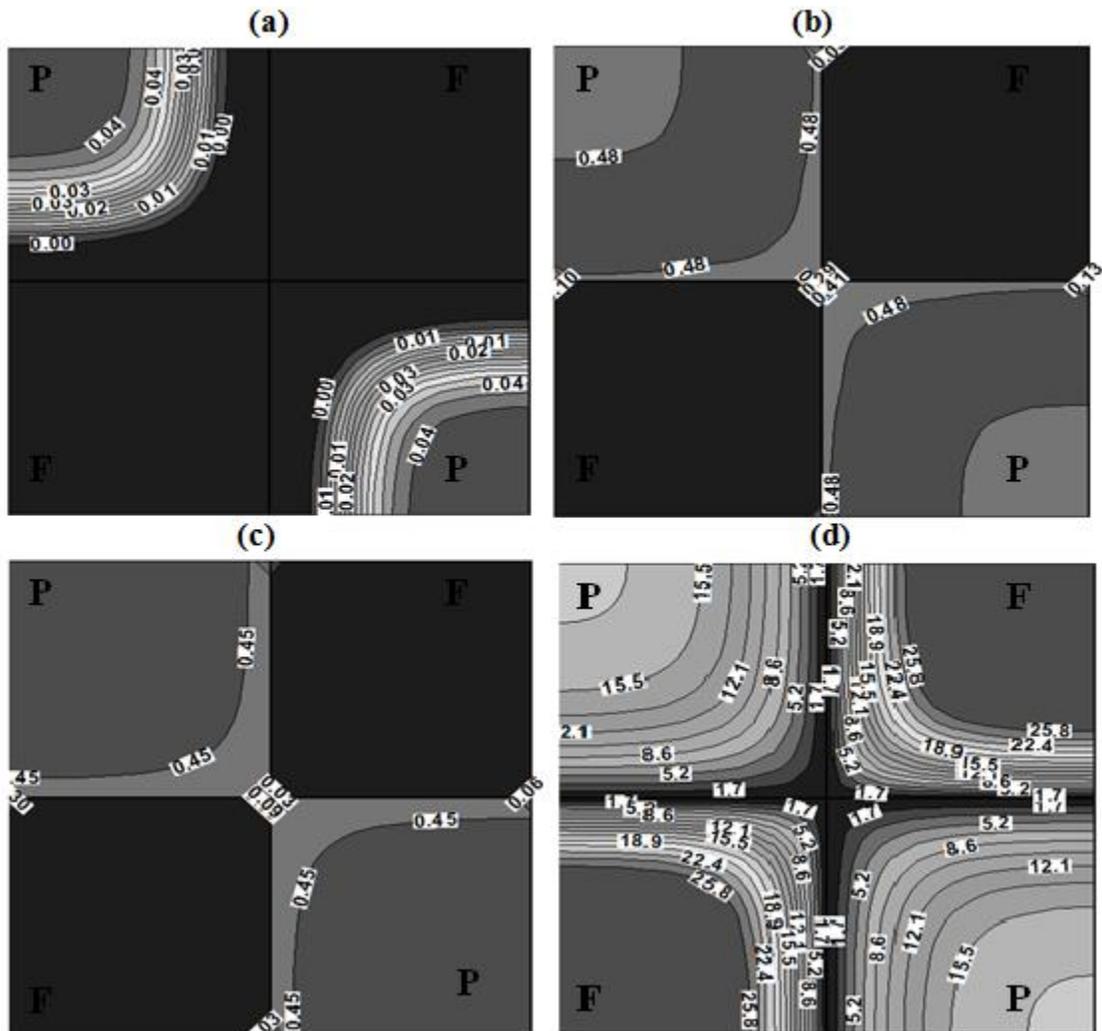


Figure 7.6 Co-current contour plots of CH_4 , H_2O , CO_2 concentrations and axial velocity, respectively, at fixed axial location of $Z=0.6$ m. a) CH_4 , b) H_2O , c) CO_2 and d) Z-Velocity.

7.3 Counter-current reactor design

Counter-current flow configuration has many advantages over co-current flow due to the effective heat transfer characteristics and uniform distribution of the oxygen permeation flux through the whole length of the reactor. In this case of counter flow configuration membrane reactor, fuel plus other diluent gases in the permeate side enter the reactor at $z=0.9$ m and feed stream, air, enters at $z=0$. Fig.7.7 shows the contour plots of temperature at different axial locations on planes normal to the flow direction. The temperature develops from 1173 at $z=0.9$ m to about 1440 K at $z=0$ m. the temperature rise in case of counter-current flow is improved much due to higher oxygen permeation flux and improvement in combustion. The combustion in this case starts early close to fuel inlet and the temperature reach its maximum rapidly as compared to co-current flow membrane reactor. However, the flame shape and position remains in the same position close to the membrane surface and the same flame shape is also obtained.

Figure 7.8, upper plot, shows the axial average temperature distribution of feed gas, membrane and permeate gas. As shown in the figure, the temperature of permeate gas develops quickly as compared to the case of co-current and reach its maximum value faster. The membrane temperature is uniform through the reactor length except at inlet and exit regions. Due to high air flow rates in the permeate sides and thus its specific heat, the feed stream temperature is lower than the temperature of membranes and permeate streams. The temperature profiles are quite important, and careful selection of the inlet conditions could lead to large improvements in ITM performance.

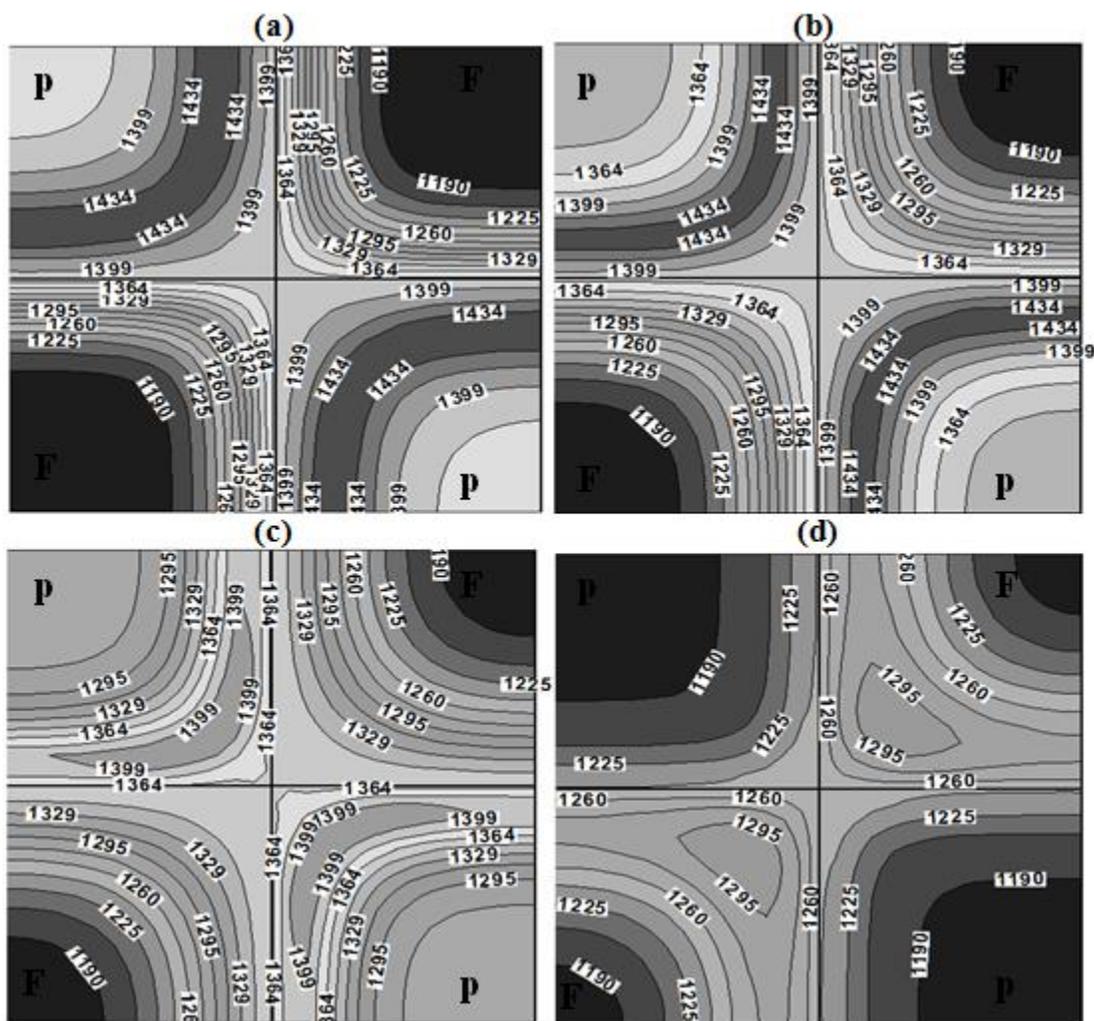


Figure 7.7 Counter-current temperature contour plots at different axial locations through the reactor. a) $Z=0.2$ m, b) $Z=0.4$ m, c) $Z=0.6$ m and d) $Z=0.8$ m.

The oxygen flux is a strong function of the local membrane temperature, and so the average membrane temperature is given for each simulation. Interestingly, the counter-current separation-only ITM has the highest average temperature due to the well-balanced heat exchange between the streams. In the lower plot, Fig.7.8, the average axial mole fractions distributions of CH_4 , CO_2 and H_2O are presented. As shown, CH_4 mole fractions starts to decline sharply after small distance from fuel inlet indicating higher oxygen permeation flux and improved combustion as compared to the smooth reduction of CH_4 through the reactor length in case of co-current reactor design. CO_2 and H_2O concentrations are increased due to combustion and after that their concentrations starts to decline due to the permeation of oxygen.

Due to effective heat transfer and oxygen permeation mechanisms in case of counter current flow, the combustion is improved and the membrane temperature is higher as compared to co-current. As shown in Fig.7.9 in the upper plot, the average flux through the reactor is higher than in case of co-current flow configuration. The oxygen permeation flux is uniform through the reactor length with a jump close to fuel inlet. This jump in oxygen flux is indicating the start of combustion and an increased membrane temperature. Examination of the partial pressure profile reveals that the partial pressure difference is essentially constant along the reactor length, indicating good material stability potential by minimizing chemical expansion stress as shown in Fig.7.9, lower plot. Another thing to note is that the oxygen mole fraction of the feed stream drops by 72.5%, indicating a high recovery ratio, and an effective ITM configuration. Further, the more sensitive region where the permeate partial pressure is low coincides with the

region where the feed partial pressure is low, which appears to be a better match-up than the co-current case, where the high feed matches up with the low permeate.

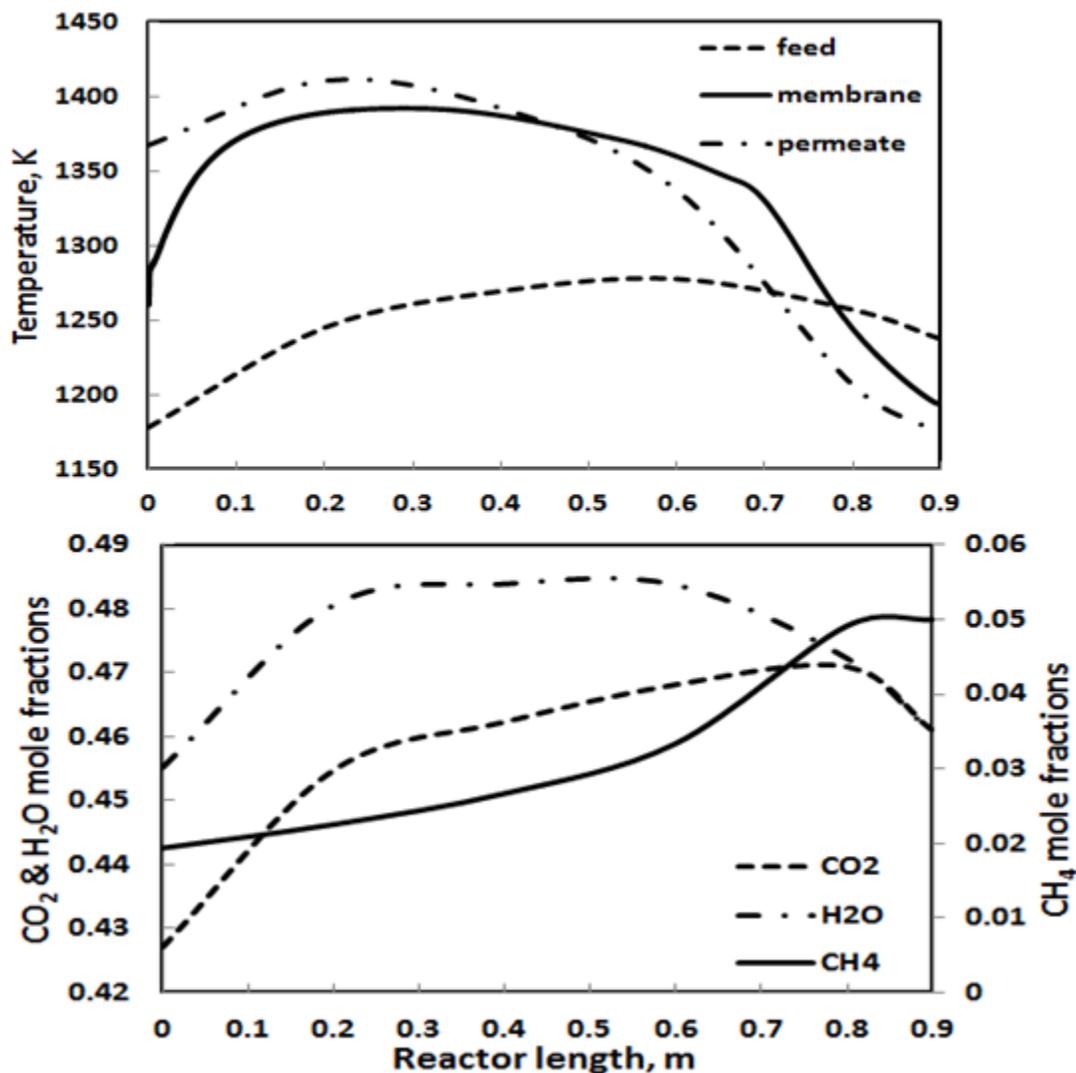


Figure 7.8 Counter-current: a) axial average temperature distribution of feed gas, membrane and permeate gas and b) axial average species mole fractions in the permeate side of the membrane.

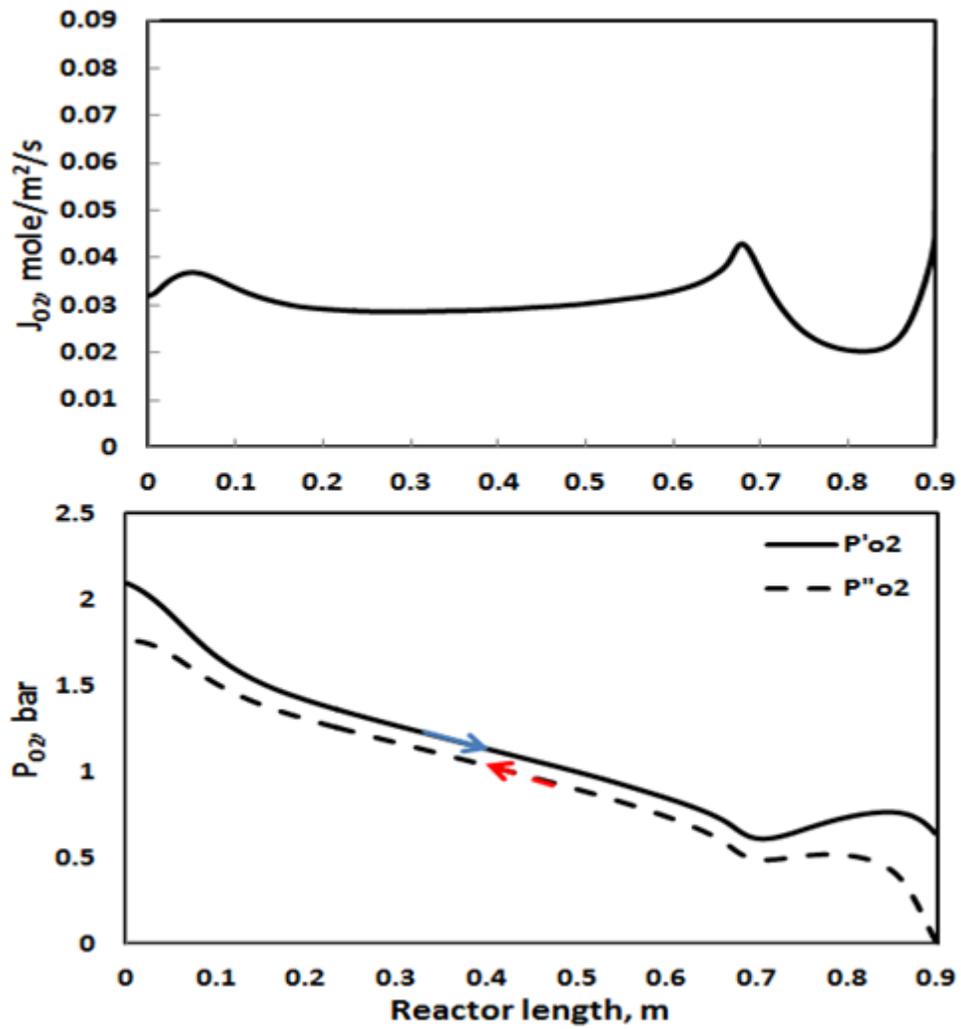


Figure 7.9 Counter-current: a) axial oxygen permeation flux distribution and b) axial local oxygen partial pressure distribution in both sides of the membrane.

Fig.7.10 shows the oxygen mole fractions distribution at different axial location s of the reactor on planes normal to the flow direction. As shown, the amount of O_2 increase in the axial direction in the permeate side and occupy larger area than the case of co-current flow which indicates higher recovery ratio.

7.4 Effect of channel width

A very important parameter regarding the ITM design is the individual monolith channel width and accordingly the reactor volume. Variations in the reactor volume have similar influences like changing the volume flow-rates. Larger reactor size results in increasing the oxygen permeation flux. However, increasing the ITM reactor size is too costly, and so there may be an optimal channel width in order to obtain a certain power output according to the limitations provided for special applications of ITM reactors. In the present study, a design of an ITM reactor is presented in order to substitute a gas turbine combustor. In this case, reactor length is limited to 0.9 m to occupy the same length as a real gas turbine combustor. The total number of channels is limited by the channel width and the available space for a real application. Modifications to the channel width directly impacts the surface area to volume ratio as well as the reactor aspect ratio, and significantly changes pressure drop for a fixed number of channels and inlet flow-rates. The channel width affects many aspects of the ITM performance, specifically the heat transfer coefficient, the surface area to volume ratio, and the local flow conditions among others. A larger channel width reactor near the inlet would result in a relatively low heat transfer coefficient, and so even if the reaction rate is small, the wall temperature could still be significantly high.

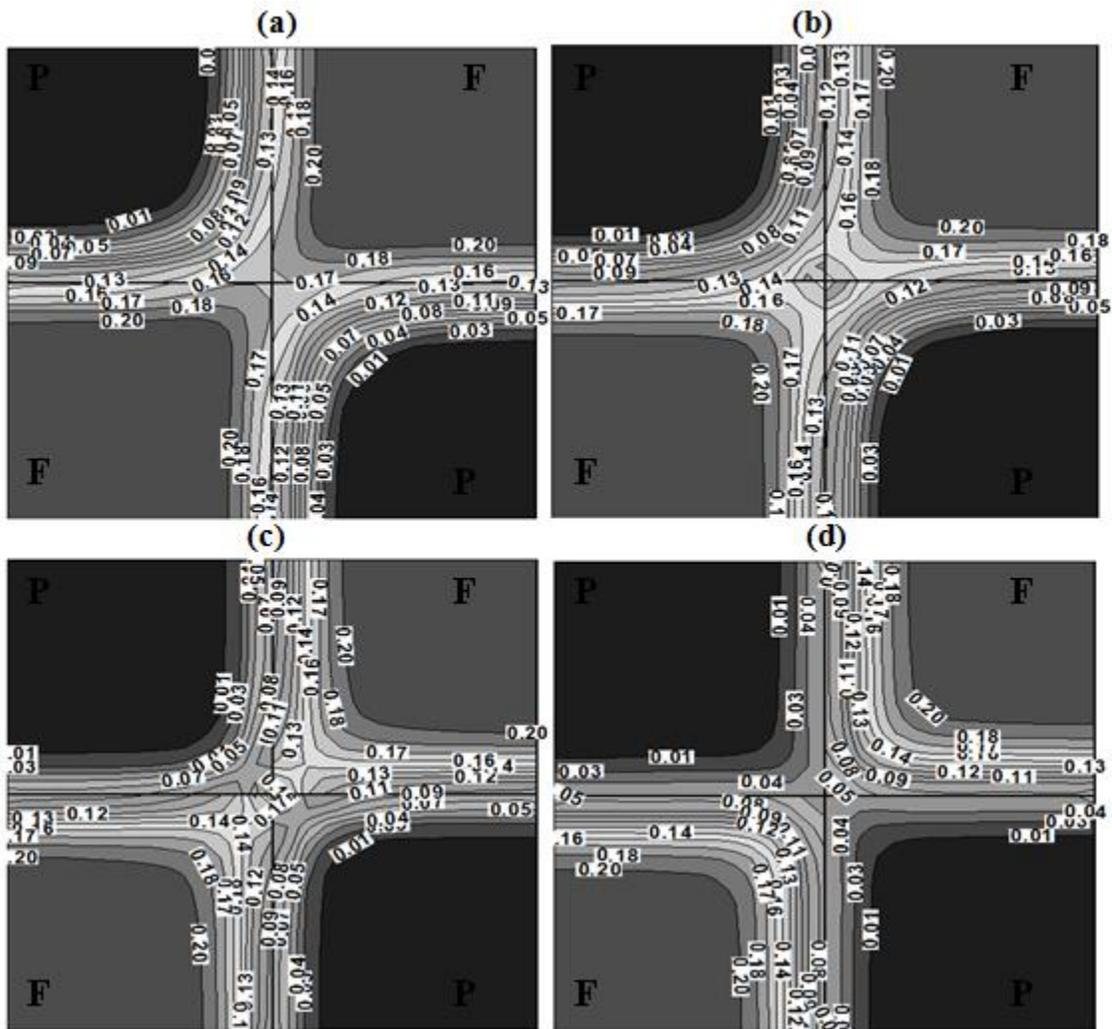


Figure 7.10 Counter-current oxygen mole fraction distribution at different axial locations through the reactor. a) $Z=0.2$ m, b) $Z=0.4$ m, c) $Z=0.6$ m and d) $Z=0.8$ m.

As a matter of fact, as the channel width is reduced, the amount of oxygen permeation flux is increased. Based on this fact, the simulations were done in order to calculate the minimum operating channel width as it is explored later in detail. It was found from the simulations that any reduction in the channel width below 15 mm results in large increases in the viscous pressure drop. Basically, as the channel width decreases, the flow velocity must increase to maintain the same mass flow-rate. The combustion also due to this high flow velocity was lost.

This analysis can be confirmed from the results in Fig.7.11 that compares the results of the minimum permissible operating channel width, 15 mm, with 20 mm channel width. Large improvement in oxygen permeation flux is obtained by reducing the channel width from 15 mm to 20 mm as shown in Fig.7.11, part (a). The temperatures are very similar in both cases and also the species concentrations. This is enough to justify the use of the minimum permissible channel width of 15 mm in the present reactor design in order to substitute a gas turbine model. By using 25,000 channels for each stream, this will result in a reactor with total volume of 10 m³.

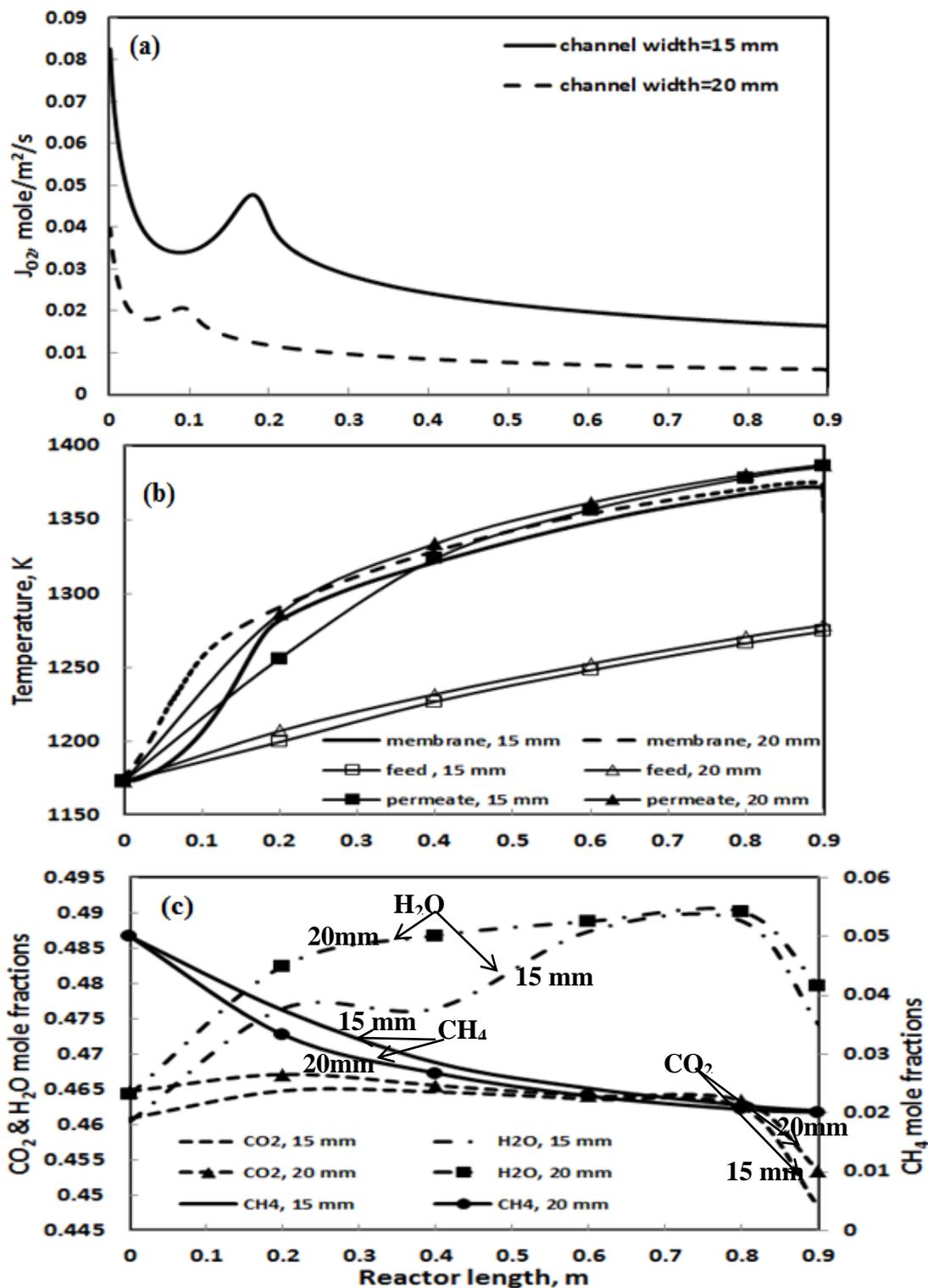


Figure 7.11 Co-current: effect of channel width on a) axial oxygen permeation flux distribution; b) axial average temperature distribution of feed gas, membrane and permeate gas ; c) axial average species mole fractions in the permeate side of the membrane.

7.5 Effect of CH₄ %

From the above results, the average membrane temperature has a significant impact on the performance of an ITM reactor. The membrane surface temperature is dependent on the intensity of combustion in the permeate sides of the membranes that accordingly depends on the percentage of fuel in the permeate sides gas flows. The amount of CH₄ in the permeate flow have two limitations, one is that, the permeate stream has an upper-bound on diluent flow-rate because the inlet methane concentration should not fall below roughly 5% for mass transfer and combustion stability reasons. Second, according to the optimization of flow rates in feed and permeate side, there is a limit for the value of oxygen permeation flux across the membrane.

At certain flow conditions like the present case, increasing the flow rates in feed and permeate sides will not result in any increase in the oxygen flux. Based on this, increasing the amount of CH₄ in the permeate side over 5% is also non-applicable because of limited oxygen permeation flux. Fig.7.12 shows the influences of reducing CH₄% in the permeate side from 5% to 2.5% Vol. with keeping H₂O% constant on oxygen permeation flux, axial average temperature distribution of feed gas, membrane and permeate gas and axial average species mole fractions in the permeate side of the membrane. As shown in the figure, part (a), better oxygen permeation flux distribution is obtained in case of 5% CH₄ as compared to the case of 2.5%. Also, the jump in oxygen permeation flux is higher in case of 5% indicating higher combustion temperature and overall improvement in the combustion process.

This may be due to the improvement in the ratio between the available oxygen for combustion and methane. However, the temperature distributions for feed gas, membrane and permeate gas are very close in both cases as shown in Fig.7.12, part (b). This may be attributed to the cooling effects of the excess permeated oxygen in the permeate side which cool down the gases. In part (c), Fig.7.12, the effects of CH₄% on the combustion process is clear and can be seen easily from the average species concentrations through the reactor. For both cases, 5% and 2.5%, the amount of H₂O at inlet is the same. However, in case of 5% CH₄, the concentrations of H₂O are much higher as compared to the case of 2.5% CH₄. This indicates an improvement in combustion process as H₂O is a combustion product. Further more, CO₂ concentrations are also improved.

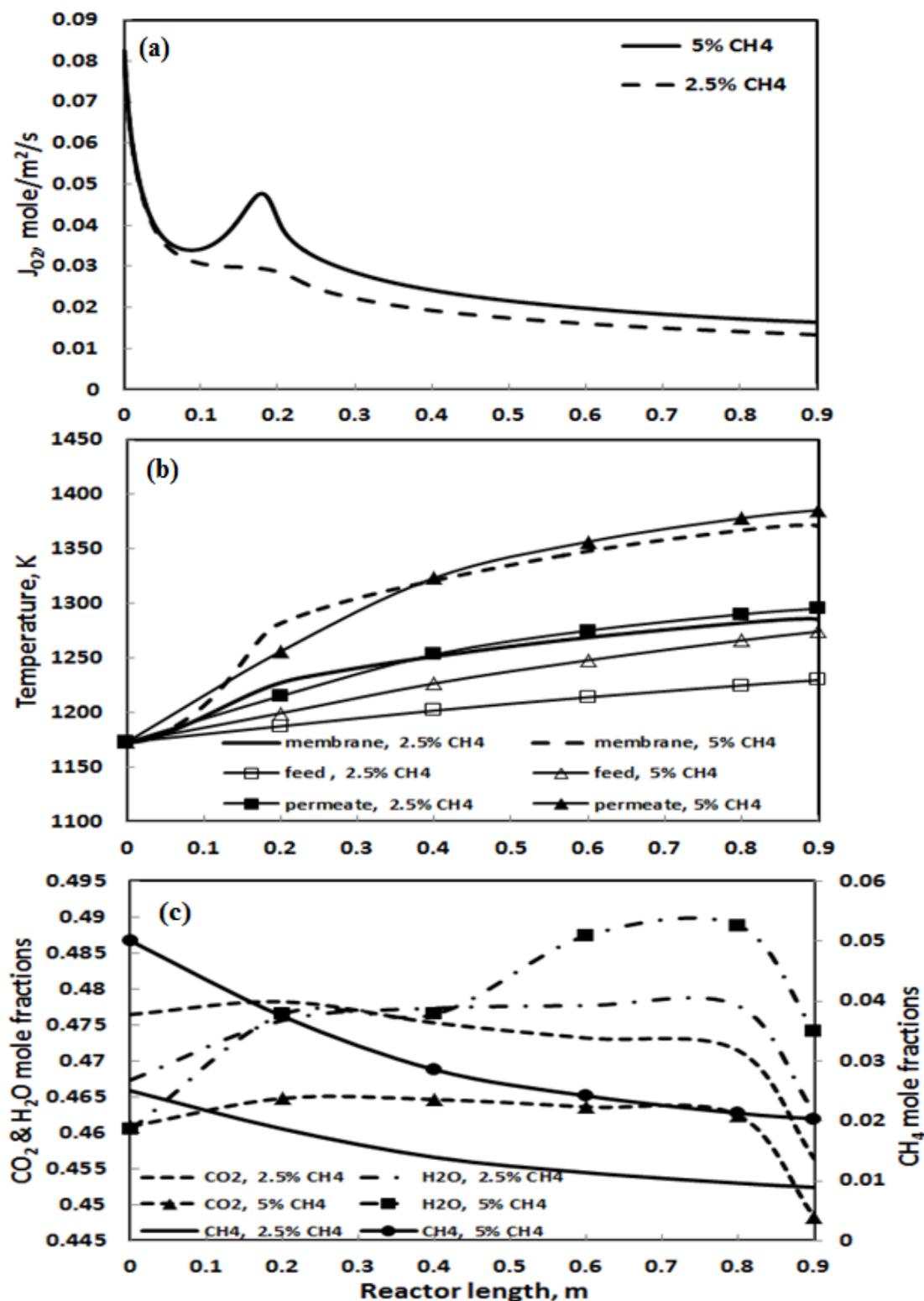


Figure 7.12 Co-current: effect of CH₄% on a) axial oxygen permeation flux distribution; b) axial average temperature distribution of feed gas, membrane and permeate gas ; c) axial average species mole fractions in the permeate side of the membrane.

In conclusion of this part of the present study, an ITM monolith structure reactor design is introduced for substituting a conventional gas turbine combustor using LSCF1991 membranes. Optimizations for the feed and sweep flow rates were performed in order to meet the power required and all simulations were conducted in 3D. Effects of flow configurations, channel width and percentage of CH_4 in the permeate side flow have been introduced under constant inlet gas temperature of 1173 K and a fixed operating pressure of 10 bars. The reactor geometry was optimized based on the optimization of channel width.

It is concluded that counter-current flow configuration design resulted in improvements in oxygen permeation flux and overall heat transfer characteristics. However, it has a limitation as a result of increased membrane temperature. Any reduction in the channel width below 15 mm resulted in large increase in the viscous pressure drop and losing the combustion due to increased flow velocity. As well, increasing the amount of CH_4 in the permeate side over 5% was found to be non-applicable because of limited oxygen permeation flux. The present ITM reactor has the capability of producing power output in the range of 5 to 8 MWe based on cycle first law efficiency.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The main objective of this work is to conduct detailed studies for investigating the two main approaches available for oxy-fuel combustion. In the first approach, Oxygen is extracted from the atmosphere using air separation units and then used in the combustion process. The second approach is based on combining air separation and combustion processes utilizing the ion transport reactor technology. To satisfy this objective regarding the application of oxy-combustion technology in conventional combustors, both experimental and numerical investigations were conducted for an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor. Oxy-combustion and emission characterization, flame stabilization and oxy-combustion model validation have been investigated in details. The combustor is fuelled with CH_4 and a mixture of CO_2 and O_2 as oxidizer. A modified two-step oxy-combustion reaction kinetics model for methane-oxygen combustion has been used in order to predict the oxy-combustion characteristics of the considered flame and validations have been done using the experimental results. Wide ranges of different operating parameters have been considered including equivalence ratio, percentage of O_2/CO_2 in the oxidizer mixture and fuel volume flow rate. The stability of the oxy-combustion diffusion flame has been checked experimentally and numerically.

Also to satisfy our objective regarding the application of oxy-combustion technology into ITM reactors, a modified two step finite rate reaction kinetics model for methane oxy-combustion has been introduced in order to predict the oxy-fuel combustion characteristics inside an ITM reactor. A detailed 2D study has been presented in the present work to understand more the performance of an ITM reactor under the oxy-combustion conditions in the permeate side of the membrane. Also, Coefficients of the oxygen permeation equation have been introduced for a LSCF1991 ion transport membrane based on the fitting of the experimental data in the literature. The analysis of the effect of reactivity on the permeation process has been discussed. The effects of many parameters including inlet gases temperature (feed and sweep), reactor geometry, feed and sweep volume flow rates, oxygen partial pressure in the feed side and the effect of the percentage of CH_4 in the sweep gases mixture on the permeation process and oxy-combustion characteristics have been analyzed.

From our understanding that came out from the above analysis of ITM reactor, a new 3D reactor design is introduced for the substitution of ITM reactors into a gas turbine combustor. An ITM monolith structure reactor design has been introduced for substituting a conventional gas turbine combustor using LSCF1991 membranes. Optimizations for the feed and sweep flow rates were performed in order to meet the power required and all simulations were conducted in 3D. Effects of flow configurations, channel width and percentage of CH_4 in the permeate side flow have been introduced under constant inlet gas temperature of 1173 K and a fixed operating pressure of 10 bars. The reactor geometry was optimized based on the optimization of channel width.

8.1 Conclusions

Based on the above detailed study, one can conclude the following:

1. The stability of the oxy-combustion flame in the gas turbine combustion application is affected when the operating percentage of Oxygen in the oxidizer mixture is reduced below 25 %. Also, no operation was possible for the burner with less than 21% Oxygen in the oxidizer mixture.
2. The combustion stability in the gas turbine combustor was found to be improved with increasing the percentage of O_2 at the inlet; however, there is a limitation in temperature. Also, by lowering the equivalence ratio, improvement in flow swirl and the overall combustion process in the gas turbine combustor were improved.
3. Both experimental and numerical results are in good agreement and the modified two step reaction kinetics model is capable of predicting very similar trends of temperature and also the overall flame shape is very close to the recorded experimental flame shape recorded for the gas turbine combustor.
4. From the 2D sensitivity analysis done above for the simple symmetric design ITM reactor, one can say that there are important parameters affecting the operation of ITM reactors (reactions are activated) like the inlet gases temperature (feed and sweep), percentage of CH_4 in the sweep gases mixture and the reactor geometry. Also, there are less important parameters such as, feed and sweep volume flow rates, and oxygen partial pressure in the feed side.

5. The 2D analysis showed that the chemical reactions have a great effect on enhancing the oxygen permeation flux.
6. Based on the 3D analysis of the monolith structure design ITM reactor for the target of substituting ITM reactor into gas turbine combustor, it is concluded that counter-current flow configuration design resulted in improvements in oxygen permeation flux and overall heat transfer characteristics. However, it has a limitation as a result of increased membrane temperature.
7. From the 3D case, it was shown that any reduction in the channel width below 15 mm resulted in large increase in the viscous pressure drop and losing the combustion due to increased flow velocity. Further, increasing the amount of CH_4 in the permeate side over 5% was found to be non-applicable because of limited oxygen permeation flux.
8. The present ITM reactor has the capability of producing power output in the range of 5 to 8 MWe based on cycle first law efficiency.

8.2 Recommendations

In the present work, the current status of the oxy-combustion technology has been discussed regarding the applications of this technology in gas turbines and ITM reactors. Experimental and numerical investigations have been conducted on a gas turbine model combustor. The stability of the flame, oxy-fuel combustion and emission characteristics and validation for the oxy-combustion reaction model has been checked. Most of the present work is regarding the ITM reactors applications. A detailed analysis for the most recent advancement in the ITM reactors technology with more analysis regarding the membrane separation mechanism, the available permeation equations in the literature and the membrane performance regarding separation only and ITM reactor applications has been discussed in the literature review part. New coefficients oxygen permeation equation model is introduced herein this work by fitting the experimental data available in the literature for a LSCF-1991 ion transport membrane. From our understandings of the oxygen permeation and oxy-fuel combustion characteristics that come out from a 2D analysis of a simple symmetric ITM reactor, a new 3D reactor design is introduced for the substitution of ITM reactors into a gas turbine combustor.

From the above discussion regarding the oxy-fuel combustion technology, we can recommend the following:

1. In the present work, an analysis oxy-combustion in a gas turbine model combustor has been conducted both experimentally and numerically without comparison with air operation as a reference case. This comparison should be the next step in both experimental and numerical work.

2. Regarding the validation of the numerical model using the experimental data, only two steps oxy-combustion reaction kinetics model has been considered. It is needed to increase the number of steps in order to consider the most important reactions inside the reactor for more accurate results.
3. Tools are required to measure the inside reactor temperature and species concentrations in order to characterize the flame in details.
4. The applications of the idea of ITM reactors in industry has a bright future specially in the power cycle applications; however more research is still needed regarding the optimization of the ITM reactors geometry and operating conditions.
5. Also, the idea of application of oxy-combustion technology into gas turbines is possible; however, the combustion temperature will be increased tremendously which need more control to safe the turbine blades.
6. More experimental work is needed in this application to gas turbines as the amount of the available work in the literature is very small and more research is required to control the combustion temperature within a certain limit below the blades material failure.
7. More research in the branch of material science is required to improve the application of oxy-fuel combustion technology in both ITM reactors and gas turbines as there are still numbers of issues regarding the behavior of membrane and turbine blades materials at higher operating temperatures.

APPENDIX A

GAS TURBINE EXPERIMENTAL OPERATING

CONDITIONS

To satisfy our objective regarding the application of oxy-combustion technology in conventional combustors, experimental investigations on an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor is conducted. The combustor is fuelled with CH_4 and a mixture of CO_2 and O_2 as oxidizer. Large operating range of parameters including equivalence ratio (from 0.5 to 1.0), percentages of O_2/CO_2 in the oxidizer mixture (from 100% till flame blow out), fuel volume flow rates (from 5 to 9 L/min) are considered in this work.

A.1 Experimental operating conditions

In this work, wide range of operating equivalence ratios has been considered. At each equivalence ratio, the fuel volume flow rate is changed from 5 to 9 L/min and at each fuel volume flow rate, the percentage of oxygen in the oxidizer mixture is changed from 100% till the flame blow out. The following table are describing those operating conditions in details, each table is showing the operating conditions at a certain operating equivalence ratio. 35 experimental sets of experiments have been considered.

TABLE A.1 Experimental operating conditions at fixed equivalence ratio of 0.5.

Experiment set number	$V^0_{CH_4}$ (L/min)	Power (kW)	$O_2\%$	$V^0_{O_2}$ (L/min)	$V^0_{CO_2}$ (L/min)
set #1	5	2.782916667	100	20	0
			80	20	5
			60	20	13.33
			50	20	20
			45	20	24.44
			40	20	30
			35	20	37.14
			30	20	46.67
set #2	6	3.3395	25	20	60
			100	24	0
			80	24	6
			60	24	16
			50	24	24
			45	24	29.33
			40	24	36
			35	24	44.57
set #3	7	3.896083333	30	24	56
			25	24	72
			100	28	0
			80	28	7
			60	28	18.67
			50	28	28
			45	28	34.22
			40	28	42
set #4	8	4.452666667	35	28	52
			30	28	65.33
			25	28	84
			100	32	0
			80	32	8
			60	32	21.33
			50	32	32
			45	32	39.11
set #5	9	5.00925	40	32	48
			35	32	59.42
			30	32	74.67
			25	32	96
			100	36	0
			80	36	9
			60	36	24
			50	36	36
45	36	44			
set #5	9	5.00925	40	36	54
			35	36	66.85
			30	36	84
set #5	9	5.00925	25	36	105
			25	36	105

TABLE A.2 Experimental operating conditions at fixed equivalence ratio of 0.55.

Experiment set number	$V^{\circ}_{\text{CH}_4}$ (L/min)	Power (kW)	$\text{O}_2\%$	$V^{\circ}_{\text{O}_2}$ (L/min)	$V^{\circ}_{\text{CO}_2}$ (L/min)
set #6	5	2.782916667	100	18.18	0
			80	18.18	4.55
			60	18.18	12.12
			50	18.18	18.18
			45	18.18	22.22
			40	18.18	27.27
			35	18.18	33.76
			30	18.18	42.42
set #7	6	3.3395	25	18.18	54.54
			100	21.81	0
			80	21.81	5.45
			60	21.81	14.54
			50	21.81	21.81
			45	21.81	26.66
			40	21.81	32.72
			35	21.81	40.52
set #8	7	3.896083333	30	21.81	50.9
			25	21.81	65.45
			100	25.45	0
			80	25.45	6.36
			60	25.45	16.97
			50	25.45	25.45
			45	25.45	31.11
			40	25.45	38.18
set #9	8	4.452666667	35	25.45	47.27
			30	25.45	59.4
			25	25.45	76.36
			100	29.1	0
			80	29.1	7.27
			60	29.1	19.4
			50	29.1	29.1
			45	29.1	35.55
set #10	9	5.00925	40	29.1	43.64
			35	29.1	54.03
			30	29.1	67.88
			25	29.1	87.27
			100	32.73	0
			80	32.73	8.18
			60	32.73	21.82
			50	32.73	32.73
45	32.73	40			
40	32.73	49.1			
35	32.73	60.78			
30	32.73	76.36			
25	32.73	98.18			

TABLE A.3 Experimental operating conditions at fixed equivalence ratio of 0.6.

Experiment set number	$V^0_{CH_4}$ (L/min)	Power (kW)	$O_2\%$	$V^0_{O_2}$ (L/min)	$V^0_{CO_2}$ (L/min)
set #11	5	2.782916667	100	16.66	0
			80	16.66	4.17
			60	16.66	11.11
			50	16.66	16.67
			45	16.66	20.37
			40	16.66	25
			35	16.66	30.95
			30	16.66	38.89
set #12	6	3.3395	25	16.66	50
			100	20	0
			80	20	5
			60	20	13.33
			50	20	20
			45	20	24.44
			40	20	30
			35	20	37.14
set #13	7	3.896083333	30	20	46.67
			25	20	60
			100	23.33	0
			80	23.33	5.83
			60	23.33	15.56
			50	23.33	23.33
			45	23.33	28.52
			40	23.33	35
set #14	8	4.452666667	35	23.33	43.33
			30	23.33	54.44
			25	23.33	70
			100	26.67	0
			80	26.67	6.67
			60	26.67	17.77
			50	26.67	26.67
			45	26.67	32.6
set #15	9	5.00925	40	26.67	40
			35	26.67	49.52
			30	26.67	62.22
			25	26.67	80
			100	30	0
			80	30	7.5
			60	30	20
			50	30	30
45	30	36.67			
40	30	45			
35	30	55.71			
30	30	70			
25	30	90			

TABLE A.4 Experimental operating conditions at fixed equivalence ratio of 0.65.

Experiment set number	$V^{\circ}_{\text{CH}_4}$ (L/min)	Power (kW)	$\text{O}_2\%$	$V^{\circ}_{\text{O}_2}$ (L/min)	$V^{\circ}_{\text{CO}_2}$ (L/min)
set #16	5	2.782916667	100	15.38	0
			80	15.38	3.85
			60	15.38	10.25
			50	15.38	15.38
			45	15.38	18.8
			40	15.38	23.07
			35	15.38	28.57
			30	15.38	35.9
set #17	6	3.3395	25	15.38	46.15
			100	18.46	0
			80	18.46	4.62
			60	18.46	12.3
			50	18.46	18.46
			45	18.46	22.56
			40	18.46	27.69
			35	18.46	34.28
set #18	7	3.896083333	30	18.46	43.07
			25	18.46	55.38
			100	21.54	0
			80	21.54	5.38
			60	21.54	14.36
			50	21.54	21.54
			45	21.54	26.32
			40	21.54	32.3
set #19	8	4.452666667	35	21.54	40
			30	21.54	50.26
			25	21.54	64.62
			100	24.62	0
			80	24.62	6.15
			60	24.62	16.4
			50	24.62	24.62
			45	24.62	30.1
set #20	9	5.00925	40	24.62	36.92
			35	24.62	45.7
			30	24.62	57.43
			25	24.62	73.84
			100	27.7	0
			80	27.7	6.92
			60	27.7	18.46
			50	27.7	27.7
45	27.7	33.85			
set #20	9	5.00925	40	27.7	41.54
			35	27.7	51.43
			30	27.7	64.62
			25	27.7	83.07

TABLE A.5 Experimental operating conditions at fixed equivalence ratio of 0.7.

Experiment set number	$V^{\circ}_{\text{CH}_4}$ (L/min)	Power (kW)	$\text{O}_2\%$	$V^{\circ}_{\text{O}_2}$ (L/min)	$V^{\circ}_{\text{CO}_2}$ (L/min)
set #21	5	2.782916667	100	14.28	0
			80	14.28	3.57
			60	14.28	9.52
			50	14.28	14.28
			45	14.28	17.46
			40	14.28	21.42
			35	14.28	26.53
			30	14.28	33.33
set #22	6	3.3395	25	14.28	42.85
			100	17.14	0
			80	17.14	4.29
			60	17.14	11.43
			50	17.14	17.14
			45	17.14	20.95
			40	17.14	25.71
			35	17.14	31.84
set #23	7	3.896083333	30	17.14	40
			25	17.14	51.43
			100	20	0
			80	20	5
			60	20	13.33
			50	20	20
			45	20	24.44
			40	20	30
set #24	8	4.452666667	35	20	37.14
			30	20	46.67
			25	20	60
			100	22.85	0
			80	22.85	5.71
			60	22.85	15.24
			50	22.85	22.86
			45	22.85	27.94
set #25	9	5.00925	40	22.85	34.29
			35	22.85	42.45
			30	22.85	53.33
			25	22.85	68.57
			100	25.7	0
			80	25.7	6.43
			60	25.7	17.14
			50	25.7	25.71
45	25.7	31.43			
40	25.7	38.57			
35	25.7	47.76			
30	25.7	60			
25	25.7	77.14			

TABLE A.6 Experimental operating conditions at fixed equivalence ratio of 0.75.

Experiment set number	$V^0_{CH_4}$ (L/min)	Power (kW)	$O_2\%$	$V^0_{O_2}$ (L/min)	$V^0_{CO_2}$ (L/min)
set #26	5	2.782916667	100	13.33	0
			80	13.33	3.33
			60	13.33	8.89
			50	13.33	13.33
			45	13.33	16.3
			40	13.33	20
			35	13.33	24.76
			30	13.33	31.11
set #27	6	3.3395	25	13.33	40
			100	16	0
			80	16	4
			60	16	10.67
			50	16	16
			45	16	19.56
			40	16	24
			35	16	29.71
set #28	7	3.896083333	30	16	37.33
			25	16	48
			100	18.67	0
			80	18.67	4.67
			60	18.67	12.44
			50	18.67	18.67
			45	18.67	22.81
			40	18.67	28
set #29	8	4.452666667	35	18.67	34.67
			30	18.67	43.56
			25	18.67	56
			100	21.33	0
			80	21.33	5.33
			60	21.33	14.22
			50	21.33	21.33
			45	21.33	26.07
set #30	9	5.00925	40	21.33	32
			35	21.33	39.62
			30	21.33	49.78
			25	21.33	64
			100	24	0
			80	24	6
			60	24	16
			50	24	24
45	24	29.33			
40	24	36			
35	24	44.57			
30	24	56			
25	24	72			

TABLE A.7 Experimental operating conditions at fixed equivalence ratio of 1.0.

Experiment set number	$V^0_{CH_4}$ (L/min)	Power (kW)	$O_2\%$	$V^0_{O_2}$ (L/min)	$V^0_{CO_2}$ (L/min)
set #31	5	2.782916667	100	10	0
			80	10	10
			60	10	6.67
			50	10	10
			45	10	12.22
			40	10	15
			35	10	18.57
			30	10	23.33
set #32	6	3.3395	25	10	30
			100	12	0
			80	12	3
			60	12	8
			50	12	12
			45	12	14.67
			40	12	18
			35	12	22.29
set #33	7	3.896083333	30	12	28
			25	12	36
			100	14	0
			80	14	3.5
			60	14	9.33
			50	14	14
			45	14	17.11
			40	14	21
set #34	8	4.452666667	35	14	26
			30	14	32.67
			25	14	42
			100	16	0
			80	16	4
			60	16	10.67
			50	16	16
			45	16	19.56
set #35	9	5.00925	40	16	24
			35	16	29.71
			30	16	37.33
			25	16	48
			100	18	0
			80	18	4.5
			60	18	12
			50	18	18
45	18	22			
40	18	27			
35	18	33.43			
30	18	42			
25	18	54			

APPENDIX B

EXPERIMENTAL RESULTS AND PROCESSED DATA SHEETS

The exhaust gas temperature is measured at the exit plan of the reactor (height of 300 mm) with R-type thermocouple from Omega which has a maximum range of 1500 °C and inserted inside a 12 inches long ceramic probe to protect it from high flame temperature. The thermocouple probe is connected to a data logger and a computer which takes the average temperature at each location during one minute. The following tables are showing the temperature measurements data at the exit section of the reactor.

Repeatability of the results was checked by repeating all tests for two times under the same conditions and taking the average value. To consider gas energy at each location, the local temperature measurements at the exit section in the radial direction are repeated and average values are calculated at each location based on energy calculations.

TABLE B.1 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.55$ and $V_f=6$

L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	1008	988	952	861
80	1004	978	945	859
60	935	935	915	839
50	900	920	919	840
40	891	916	901	811
30	890	889	875	808
25	891	888	858	797

TABLE B.2 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.55$ and $V_f=9$

L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	1088	1082	1035	881
80	997	1036	994	872
60	1055	1072	1038	912
50	1056	1087	1072	959
40	1024	1047	1037	950
30	992	1005	989	867

TABLE B.3 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.65$ and $V_f=6$ L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	1078	1040	958	746
80	952	927	885	728
60	883	863	829	687
50	878	873	811	689
40	890	884	847	688
30	905	898	867	712
25	919	906	878	714

TABLE B.4 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.65$ and $V_f=9$ L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	1048	1032	998	838
80	985	983	958	801
60	1086	1073	1044	862
50	1059	1048	1027	849
40	1036	1022	1003	827
30	1023	1011	976	813
25	1017	1008	967	808

TABLE B.5 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.75$ and $V_f=6$ L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	764	760	738	642
80	764	750	723	620
60	753	737	700	590
50	798	803	771	662
40	814	823	804	686

TABLE B.6 Radial temperature data in °C at the exit section of the reactor for different concentrations of oxygen in the oxidizer mixture at $\Phi=0.75$ and $V_f=9$ L/min.

O₂ %	Radius, mm			
	0.0	10	20	30
100	901	885	872	783
80	889	887	867	738
60	912	909	884	738
50	949	943	922	778
40	923	915	885	746
30	902	897	879	723

TABLE B.7 Energy based average temperature data at the exit section of the reactor at different operating equivalence ratios for 60% O₂ in the oxidizer and

V_f=6 L/min.

Φ	T_{avg}, K	T_{avg}, °C
0.50	1181.877	908.727
0.55	1157.403	884.2533
0.60	1070.61	797.4601
0.65	1042.009	768.8589
0.70	950.7207	677.5707
0.75	929.211	656.061

TABLE B.8 Energy based average temperature data at the exit section of the reactor at different operating equivalence ratios for 60% O₂ in the oxidizer and

V_f=9 L/min.

Φ	T_{avg}, K	T_{avg}, °C
0.50	1237.118	963.968
0.55	1258.617	985.4667
0.60	1262.382	989.2317
0.65	1236.085	962.9348
0.70	1177.601	904.451
0.75	1093.121	819.9709

TABLE B.9 Energy based average temperature data at the exit section of the reactor for different oxygen concentrations in the oxidizer at $\Phi=0.55$ and $V_f=6$

L/min.

O₂ %	T_{avg}, K	T_{avg}, °C
100	1190.787	917.6371
80	1185.741	912.5915
60	1157.403	884.2533
50	1155.741	882.5914
40	1135.164	862.0141
30	1120.471	847.3206
25	1109.494	836.344

TABLE B.10 Energy based average temperature data at the exit section of the reactor for different oxygen concentrations in the oxidizer at $\Phi=0.55$ and $V_f=9$

L/min.

Φ	T_{avg}, K	T_{avg}, °C
100	1244.486	971.3355
80	1217.547	944.3965
60	1258.617	985.4667
50	1295.068	1021.918
40	1271.738	998.5884
30	1208.197	935.047

APPENDIX C

EXPERIMENTAL SETUP AND INSTRUMENTS

In this appendix, the experimental setup for the gas turbine model combustor is shown through series of photographs explaining the used instruments and techniques in order to generate the results.

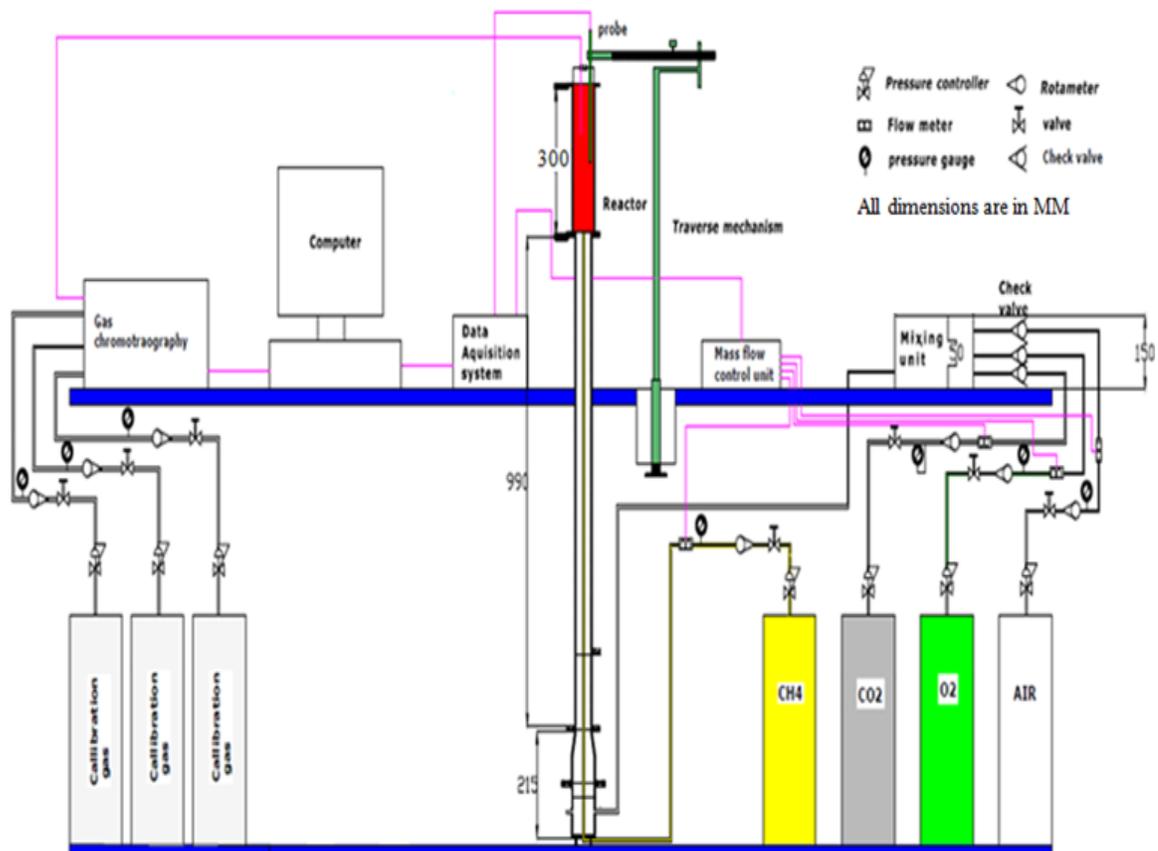


Figure C.1 Schematic diagram of the test-rig facility used in the present study.



Figure C.2 Photograph for the test-rig facility used in the present study.



Figure C.3 Photograph for the data acquisition system and post processing computers.



Figure C.4 Photograph for the mass flow controllers of CH₄, O₂, CO₂ and Air.



Figure C.5 Photograph for the mass flow meters, Rotameters, used for visualization of the flow and also for double checking of the volume flow rates.



Figure C.6 Photograph for the traverse mechanism used for fixing probes at the required position inside the reactor.



Figure C.7 Photograph for the CH₄, O₂, CO₂ and Air cylinders.



Figure C.8 Photograph for the gas chromatograph used in emission analysis and its calibration cylinders.

APPENDIX D

VISUAL C++ USER DEFINED FUNCTIONS CODES

The species transport across the membrane is carried out using a source/sink term. The source/sink term (S_i) accounts for the mass flow of species across the membrane. At the membrane boundary cells, the species are allowed to disappear from one side of the membrane through the sink term and to come out on the other side through the source term. With this method, the velocity and the pressure fields of the gas mixture are obtained from the numerical solution of the mass and momentum conservation equations, while the species concentration distribution and the relevant permeate and retentate fluxes are obtained from a scalar convection-diffusion equation including a source term to tackle the mass flow of the species across the membrane.

Transport of O_2 across the membrane was achieved using series of user-defined functions (UDF) that are written in VC++ and compiled and hooked to the FLUENT software. The following are the 2D and 3D user defined functions used in the present study written in visual C++.

D.1 Visual C++ 2D user defined function

```
/**** UDF for Oxygen permeation *****/
```

```
#include "udf.h"

#define WALLSIDE1 6

#define WALLSIDE2 16

#define P_0 101325

#define UDM_NEIGHBOUR_C 0

#define UDM_NEIGHBOUR_TC 1

#define UDM_MASS_SOURCE 2

#define UDM_flux 3

#define UDM_PP 4

#define TOLERANCE 1E-10

#define SPECIES_NUMBER 0

DEFINE_INIT(init_function,d)

{

    Thread *tc1, *tc2;

    Thread *tf1, *tf2;

    cell_t c1, c2;

    face_t f1, f2;

    real f_c1[2], f_c2[2];

    thread_loop_c(tc1,d)

    {

        begin_c_loop(c1,tc1)

        {

            C_UDMI(c1,tc1,UDM_NEIGHBOUR_C) = 0.0;
```

```

    C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC) = 0.0;
    C_UDMI(c1,tc1,UDM_MASS_SOURCE) = 0.0;
}
end_c_loop(c1,tc1)
}
tf1 = Lookup_Thread(d,WALLSIDE1);
tf2 = Lookup_Thread(d,WALLSIDE2);
begin_f_loop(f1,tf1)
{

    F_CENTROID(f_c1,f1,tf1);
    c1 = F_C0(f1,tf1);
    tc1 = THREAD_T0(tf1);
    begin_f_loop(f2,tf2)
    {
        F_CENTROID(f_c2,f2,tf2);
        if (fabs(f_c1[0]-f_c2[0]) <= TOLERANCE &&
            fabs(f_c1[1]-f_c2[1]) <= TOLERANCE )
        {
            c2 = F_C0(f2,tf2);
            tc2 = THREAD_T0(tf2);
            C_UDMI(c1,tc1,UDM_NEIGHBOUR_C) = c2 + 0.1;
            C_UDMI(c2,tc2,UDM_NEIGHBOUR_C) = c1 + 0.1;

```

```

    C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC) = THREAD_ID(tc2) + 0.1;
    C_UDMI(c2,tc2,UDM_NEIGHBOUR_TC) = THREAD_ID(tc1) + 0.1;
}
}
end_f_loop(f2,tf2)
}
end_f_loop(f1,tf1)
Message("\n Membrane initialisation completed.\n");
}
DEFINE_SOURCE(source_mass,c,t,ds,eqn)
{
ds[eqn] = 0.;
return C_UDMI(c,t,UDM_MASS_SOURCE);
}
DEFINE_ADJUST(adjust_sources, d)
{
Thread *tc1, *tc2;
Thread *tf1;
cell_t c1, c2;
face_t f1;
real mass_flux, face_area, face_area_vector[3];
real massfrac1_O2, massfrac1_N2,massfrac1_CH4, massfrac1_CO2,
massfrac1_H2O,massfrac1_H2,massfrac1_CO, cell_volume1;

```

```
real massfrac2_O2, massfrac2_N2, massfrac2_CH4, massfrac2_CO2,
massfrac2_H2O, massfrac2_H2, massfrac2_CO, cell_volume2;

real molefrac1_O2, molefrac2_O2;

real O2_mwt, N2_mwt, H2O_mwt, CO2_mwt, CH4_mwt, H2_mwt, CO_mwt;

real P1, P2, PP1, PP2;

real L, kr, kf, Dv;

CH4_mwt = 16.0026;

O2_mwt = 31.9988;

CO2_mwt = 44.00995;

N2_mwt = 28.0134;

H2O_mwt = 18.01534;

H2_mwt = 2.01594;

CO_mwt = 28.01055;

L = 0.9e-03;

tf1 = Lookup_Thread(d, WALLSIDE1);

begin_f_loop(f1, tf1)
{
F_AREA(face_area_vector, f1, tf1);

face_area = NV_MAG(face_area_vector);

c1 = F_C0(f1, tf1);

tc1 = THREAD_T0(tf1);

cell_volume1 = C_VOLUME(c1, tc1);

c2 = (int)C_UDMI(c1, tc1, UDM_NEIGHBOUR_C);
```

```
tc2 = Lookup_Thread(d, (int)C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC));
```

```
cell_volume2 = C_VOLUME(c2,tc2);
```

```
massfrac1_CH4 = C_YI(c1,tc1,0);
```

```
massfrac2_CH4 = C_YI(c2,tc2,0);
```

```
massfrac1_O2 = C_YI(c1,tc1,1);
```

```
massfrac2_O2 = C_YI(c2,tc2,1);
```

```
massfrac1_CO2 = C_YI(c1,tc1,2);
```

```
massfrac2_CO2 = C_YI(c2,tc2,2);
```

```
massfrac1_H2O = C_YI(c1,tc1,3);
```

```
massfrac2_H2O = C_YI(c2,tc2,3);
```

```
massfrac1_H2 = C_YI(c1,tc1,4);
```

```
massfrac2_H2 = C_YI(c2,tc2,4);
```

```
massfrac1_CO = C_YI(c1,tc1,5);
```

```
massfrac2_CO = C_YI(c2,tc2,5);
```

```
massfrac1_N2 = C_YI(c1,tc1,6);
```

```
massfrac2_N2 = C_YI(c2,tc2,6);
```

```
molefrac1_O2 =
```

```
(massfrac1_O2/O2_mwt)/((massfrac1_O2/O2_mwt)+(massfrac1_N2/N2_mwt)+(massfrac1_CH4/CH4_mwt)+(massfrac1_CO2/CO2_mwt)+(massfrac1_H2O/H2O_mwt)+(massfrac1_H2/H2_mwt)+(massfrac1_CO/CO_mwt));
```

```

molefrac2_O2 =
(massfrac2_O2/O2_mwt)/((massfrac2_O2/O2_mwt)+(massfrac2_N2/N2_mwt)+(massfra
c2_CH4real mass_flux, face_area, face_area_vector[3]);
real massfrac1_O2, massfrac1_N2,massfrac1_CH4, massfrac1_CO2,
massfrac1_H2O,massfrac1_H2,massfrac1_CO, cell_volume1;
real massfrac2_O2, massfrac2_N2,massfrac2_CH4, massfrac2_CO2,
massfrac2_H2O,massfrac2_H2,massfrac2_CO, cell_volume2;

real molefrac1_O2, molefrac2_O2;

real O2_mwt, N2_mwt,H2O_mwt,CO2_mwt,CH4_mwt,H2_mwt,CO_mwt;

real P1, P2, PP1, PP2;

real L, kr, kf, Dv;

CH4_mwt = 16.0026;

O2_mwt = 31.9988;

CO2_mwt = 44.00995;

N2_mwt = 28.0134;

H2O_mwt = 18.01534;

H2_mwt = 2.01594;

CO_mwt = 28.01055;

L = 0.9e-03;

massfrac1_CH4 = C_YI(c1,tc1,0);

    massfrac2_CH4 = C_YI(c2,tc2,0);

    massfrac1_O2 = C_YI(c1,tc1,1);

    massfrac2_O2 = C_YI(c2,tc2,1);

```

$$\text{massfrac1_CO2} = \text{C_YI}(c1,tc1,2);$$

$$\text{massfrac2_CO2} = \text{C_YI}(c2,tc2,2);$$

$$\text{massfrac1_H2O} = \text{C_YI}(c1,tc1,3);$$

$$\text{massfrac2_H2O} = \text{C_YI}(c2,tc2,3);$$

$$\text{massfrac1_H2} = \text{C_YI}(c1,tc1,4);$$

$$\text{massfrac2_H2} = \text{C_YI}(c2,tc2,4);$$

$$\text{massfrac1_CO} = \text{C_YI}(c1,tc1,5);$$

$$\text{massfrac2_CO} = \text{C_YI}(c2,tc2,5);$$

$$\text{massfrac1_N2} = \text{C_YI}(c1,tc1,6);$$

$$\text{massfrac2_N2} = \text{C_YI}(c2,tc2,6);$$

$$\text{molefrac1_O2} =$$

$$\frac{(\text{massfrac1_O2/O2_mwt})}{((\text{massfrac1_O2/O2_mwt})+(\text{massfrac1_N2/N2_mwt})+(\text{massfrac1_CH4/CH4_mwt})+(\text{massfrac1_CO2/CO2_mwt})+(\text{massfrac1_H2O/H2O_mwt})+(\text{massfrac1_H2/H2_mwt})+(\text{massfrac1_CO/CO_mwt}))};$$

$$\text{molefrac2_O2} =$$

$$\frac{(\text{massfrac2_O2/O2_mwt})}{((\text{massfrac2_O2/O2_mwt})+(\text{massfrac2_N2/N2_mwt})+(\text{massfrac2_CH4/CH4_mwt})+(\text{massfrac2_CO2/CO2_mwt})+(\text{massfrac2_H2O/H2O_mwt})+(\text{massfrac2_H2/H2_mwt})+(\text{massfrac2_CO/CO_mwt}))};$$

$$P1 = \text{molefrac1_O2}*(\text{C_P}(c1,tc1)+P_0);$$

$$P2 = \text{molefrac2_O2}*(\text{C_P}(c2,tc2)+P_0);$$

```

PP1=P1;

PP2=P2;

kf = 0.35 * 100000000 * exp(-27289.8/C_T(c1,tc1));

kr = 38.5*32 * 10000000 * exp(-29021.7/C_T(c1,tc1));

Dv = 1.58 * 10e-5 * exp(-8851.7/C_T(c1,tc1));

mass_flux = face_area * ((kr * Dv * (pow(PP1,0.5)-pow(PP2,0.5)))/((2 * L * kf *
pow(PP2,0.5) * pow(PP1,0.5))+((pow(PP1,0.5) + pow(PP2,0.5)) * Dv)))));

C_UDMI(c1,tc1,UDM_MASS_SOURCE) = -mass_flux / cell_volume1;
C_UDMI(c2,tc2,UDM_MASS_SOURCE) = +mass_flux / cell_volume2;
C_UDMI(c2,tc2,UDM_flux) = mass_flux;
C_UDMI(c1,tc1,UDM_PP) = PP1;
C_UDMI(c2,tc2,UDM_PP) = PP2;
}

end_f_loop(f1,tf1)
}

```

D.2 Visual C++ 3D used defined function

```

#include "udf.h"

#define WALLSIDE1 13

#define WALLSIDE2 33

```

```
#define P_0 101325

#define UDM_NEIGHBOUR_C 0

#define UDM_NEIGHBOUR_TC 1

#define UDM_MASS_SOURCE 2

#define UDM_flux 3

#define TOLERANCE 1E-10

#define SPECIES_NUMBER 0

DEFINE_INIT(init_functionupper,d)

{

  Thread *tc1, *tc2;

  Thread *tf1, *tf2;

  cell_t c1, c2;

  face_t f1, f2;

  real f_c1[3], f_c2[3];

  thread_loop_c(tc1,d)

  {

    begin_c_loop(c1,tc1)

    {

      C_UDMI(c1,tc1,UDM_NEIGHBOUR_C) = 0.0;

      C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC) = 0.0;

      C_UDMI(c1,tc1,UDM_MASS_SOURCE) = 0.0;

    }

    end_c_loop(c1,tc1)
```

```

}

tf1 = Lookup_Thread(d,WALLSIDE1);
tf2 = Lookup_Thread(d,WALLSIDE2);
begin_f_loop(f1,tf1)
{
    F_CENTROID(f_c1,f1,tf1);
    c1 = F_C0(f1,tf1);
    tc1 = THREAD_T0(tf1);
    begin_f_loop(f2,tf2)
    {
        F_CENTROID(f_c2,f2,tf2);
        if (fabs(f_c1[0]-f_c2[0]) <= TOLERANCE &&
            fabs(f_c1[1]-f_c2[1]) <= TOLERANCE &&
            fabs(f_c1[2]-f_c2[2]) <= TOLERANCE )
        {
            c2 = F_C0(f2,tf2);
            tc2 = THREAD_T0(tf2);

            C_UDMI(c1,tc1,UDM_NEIGHBOUR_C) = c2 + 0.1;
            C_UDMI(c2,tc2,UDM_NEIGHBOUR_C) = c1 + 0.1;
            C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC) = THREAD_ID(tc2) + 0.1;
            C_UDMI(c2,tc2,UDM_NEIGHBOUR_TC) = THREAD_ID(tc1) + 0.1;
        }
    }
}

```

```

    }
}
end_f_loop(f2,tf2)
}
end_f_loop(f1,tf1)
Message("\n Membrane initialisation completed.\n");
}
DEFINE_SOURCE(source_massupper,c,t,ds,eqn)
{
    ds[eqn] = 0.0;
    return C_UDMI(c,t,UDM_MASS_SOURCE);
}
DEFINE_ADJUST(adjust_sourcesupper, d)
{
    Thread *tc1, *tc2;
    Thread *tf1;
    cell_t c1, c2;
    face_t f1;
    real mass_flux, face_area, face_area_vector[3];
    real massfrac1_O2, massfrac1_N2,massfrac1_CH4, massfrac1_CO2,
massfrac1_H2O,massfrac1_H2,massfrac1_CO, cell_volume1;
    real massfrac2_O2, massfrac2_N2,massfrac2_CH4, massfrac2_CO2,
massfrac2_H2O,massfrac2_H2,massfrac2_CO, cell_volume2;

```

```
real molefrac1_O2, molefrac2_O2;

real O2_mwt, N2_mwt, H2O_mwt, CO2_mwt, CH4_mwt, H2_mwt, CO_mwt;

real P1, P2, PP1, PP2;

real L, kr, kf, Dv;

CH4_mwt = 16.0026;

O2_mwt = 31.9988;

CO2_mwt = 44.00995;

N2_mwt = 28.0134;

H2O_mwt = 18.01534;

H2_mwt = 2.01594;

CO_mwt = 28.01055;

L = 0.9e-03;

massfrac1_CH4 = C_YI(c1,tc1,0);

    massfrac2_CH4 = C_YI(c2,tc2,0);

    massfrac1_O2 = C_YI(c1,tc1,1);

    massfrac2_O2 = C_YI(c2,tc2,1);

    massfrac1_CO2 = C_YI(c1,tc1,2);

    massfrac2_CO2 = C_YI(c2,tc2,2);

    massfrac1_H2O = C_YI(c1,tc1,3);

    massfrac2_H2O = C_YI(c2,tc2,3);

    massfrac1_H2 = C_YI(c1,tc1,4);

    massfrac2_H2 = C_YI(c2,tc2,4);

    massfrac1_CO = C_YI(c1,tc1,5);
```

```

massfrac2_CO = C_YI(c2,tc2,5);
massfrac1_N2 = C_YI(c1,tc1,6);
massfrac2_N2 = C_YI(c2,tc2,6);
tf1 = Lookup_Thread(d,WALLSIDE1);
begin_f_loop(f1,tf1)
{
    F_AREA(face_area_vector,f1,tf1);
    face_area = NV_MAG(face_area_vector);
    c1 = F_C0(f1,tf1);
    tc1 = THREAD_T0(tf1);
    cell_volume1 = C_VOLUME(c1,tc1);
    c2 = (int)C_UDMI(c1,tc1,UDM_NEIGHBOUR_C);
    tc2 = Lookup_Thread(d, (int)C_UDMI(c1,tc1,UDM_NEIGHBOUR_TC));
    cell_volume2 = C_VOLUME(c2,tc2);
molefrac1_O2 =
(massfrac1_O2/O2_mwt)/((massfrac1_O2/O2_mwt)+(massfrac1_N2/N2_mwt)+(massfrac1_CH4/CH4_mwt)+(massfrac1_CO2/CO2_mwt)+(massfrac1_H2O/H2O_mwt)+(massfrac1_H2/H2_mwt)+(massfrac1_CO/CO_mwt));
molefrac2_O2 =
(massfrac2_O2/O2_mwt)/((massfrac2_O2/O2_mwt)+(massfrac2_N2/N2_mwt)+(massfrac2_CH4
/CH4_mwt)+(massfrac2_CO2/CO2_mwt)+(massfrac2_H2O/H2O_mwt)+(massfrac2_H2
/H2_mwt)+(massfrac2_CO/CO_mwt));

```

```

P1 = molefrac1_O2*(C_P(c1,tc1)+P_0);
P2 = molefrac2_O2*(C_P(c2,tc2)+P_0);

PP1=P1;

PP2=P2;

kf = 0.35 * 100000000 * exp(-27289.8/C_T(c1,tc1));

kr = 38.5*32 * 10000000 * exp(-29021.7/C_T(c1,tc1));

Dv = 1.58 * 10e-5 * exp(-8851.7/C_T(c1,tc1));

mass_flux = face_area * ((kr * Dv * (pow(PP1,0.5)-pow(PP2,0.5)))/((2 * L * kf *
pow(PP2,0.5) * pow(PP1,0.5))+((pow(PP1,0.5) + pow(PP2,0.5)) * Dv)))));

C_UDMI(c1,tc1,UDM_MASS_SOURCE) = -mass_flux / cell_volume1;

C_UDMI(c2,tc2,UDM_MASS_SOURCE) = +mass_flux / cell_volume2;

C_UDMI(c2,tc2,UDM_flux) = mass_flux;

}

end_f_loop(f1,tf1)

}

```

APPENDIX E

LIST OF PUBLICATIONS OUT OF THE PHD PROGRAM

The following papers are developed from the current PhD program. Some of them are published already, some others are submitted to journals and they are under review process right now and the rest are to be submitted shortly.

E.1 List of patents

- [1] Nemitallah M.A., Habib M.A., Ben Mansour R., Controllable temperature ITM reactor via conductive plates, “*Pat. Applied For*” the U.S. Patent and Trademark Office (USPTO) 2013, Patent Application Filed, Docket # 34000.74.

E.2 List of journal papers

1. Nemitallah M.A., Habib M.A., Ben Mansour R., Investigations of oxy-fuel combustion and oxygen permeation in an ITM reactor using a two-step oxy-combustion reaction kinetics model, *Journal of Membrane Science* 2013, 432, 1–12.
2. Ben-Mansour R., Habib M. , Badr H., Uddin A., Nemitallah M.A., Characteristics of Oxy-fuel Combustion in an Oxygen Transport Reactor, *Energy Fuels*. 2012, dx.doi.org/10.1021/ef300539c *Energy Fuels* 2012, 26, 4599–4606.
3. Habib M.A., Nemitallah M.A., Ben-Mansour R., Recent Development in Oxy-Combustion Technology and Its Applications to Gas Turbine Combustors and ITM Reactors, dx.doi.org/10.1021/ef301266j | *Energy Fuels* 2013, 27, 2–19.
4. Habib M.A., Ben-Mansour R., Nemitallah M.A., Modeling of Oxygen permeation through a LSCF ion transport membrane, *J. Computers and Fluids* 2013, 10.1016/j.compfluid.2013.01.007.

5. Ben-Mansour R., Habib M.A., Nemitallah M.A., Rajhi M., Suara K. A., characteristics of oxyfuel air fuel combustion in an industrial water tube boiler, journal of heat transfer engineering 2013, accepted paper.
6. Nemitallah M.A., Habib M.A., Ben Mansour R., Investigations of an ion transport membrane reactor specially designed for a power cycle, Applied Mechanics and Materials 2013, Vol. 302 (2013), 440-446.
7. Nemitallah M.A., Habib M.A., Ben Mansour R., Investigations of oxy-fuel combustion characteristics and oxygen permeation process in a stagnation flow ITM reactor, Applied Mechanics and Materials 2013, Vol. 302 (2013), 35-41.
8. Nemitallah M.A., Elnakla M., Fluid to fluid modeling for post dry out using dimensional analysis and energy scaling, Applied Mechanics and Materials Vol. 302 (2013) pp 42-48.
9. Ben Mansour R., Nemitallah M.A., Habib M.A., Numerical Investigations of oxygen permeation and methane-oxycombustion in a stagnation flow ion transport membrane reactor, ENERGY 2013, 10.1016/j.energy.2013.03.027.
10. Nemitallah M.A., Habib M.A., Ben Mansour R., Experimental and numerical investigations of an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor: oxy-combustion and emission characterization, flame stabilization and model validation, Applied Energy 2013, APEN-D-12-03911, under review.
11. Mohamed A. Habib, Medhat A. Nemitallah, Mostafa H. Sharqawy, Perveez Ahmad, Inam Guhlam and Mohammed Yaqub, Experimental investigations of an atmospheric diffusion oxy-combustion flame in a gas turbine model combustor, Experimental thermal and fluid science 2013, under review.
12. Nemitallah M.A., Habib M.A., Ben Mansour R., Substitution of ion transport membrane reactors into gas turbine combustors, Journal of membrane science, under review.

E.3 List of conference papers

- [1] Nemitallah M.A., Ben Mansour R., Habib M.A., Numerical investigations of methane fueled oxy-fuel combustion model in a gas turbine combustor: 1.Flow

fields, temperature, and species distribution 2. Effect of CO₂ recirculation, proceeding of the 10th WSEAS International Conference on Heat Transfer, Thermal Engineering and Environment (HTE '12), Istanbul, Turkey, August 21-23, 2012, ISSN: 2227-4596 and ISBN: 978-1-61804-114-2.

- [2] Ben-Mansour R., Habib M.A., Nemitallah M.A., Rajhi M., Suara K. A., characteristics of oxyfuel air fuel combustion in an industrial water tube boiler, HEFAT2012, proceedings of the 9th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics 16 – 18 July 2012, Malta.

- [3] Nemitallah M.A., Habib M.A., Ben Mansour R., Investigations of an ion transport membrane reactor specially designed for a power cycle, proceedings of the 2nd International Conference on Mechanical Engineering and Materials, Sanya, China, January 27-28, 2013, paper ID: 39.

- [4] Nemitallah M.A., Habib M.A., Ben Mansour R., Investigations of oxy-fuel combustion characteristics and oxygen permeation process in a stagnation flow ITM reactor, proceedings of the 2nd International Conference on Mechanical Engineering, Sanya, China, January 27-28, 2013, paper ID: 40.

- [5] Nemitallah M.A., Elnakla M., Fluid to fluid modeling for post dry out using dimensional analysis and energy scaling, proceedings of the 2nd International Conference on Mechanical Engineering and Materials, Sanya, China, January 27-28, 2013, paper ID: 41.

- [6] Nemitallah M.A., Mokhiemer E., Investigations of fluid flow, heat transfer, and entropy generation for mixed convection in a vertical channel with transverse fin array, 2nd International Conference on Mechanical Engineering and Mechatronics (ICMEM'13) to be held August 8-10, 2013 in Toronto, Canada, under review.

- [7] Nemitallah M.A., Mokhiemer E., Effect of heat transfer by radiation on the fluid flow, heat transfer characteristics and best fin height in a vertical channel with transverse fin array, 2nd International Conference on Mechanical Engineering and Mechatronics (ICMEM'13) to be held August 8-10, 2013 in Toronto, Canada, under review.

NOMENCLATURE

Symbol	Designation	Units
A_c	Computational cell area	$[m^2]$
ASU	Air separation unit	[-]
CFD	computational fluid dynamics	[-]
CCS	Carbon Capture and Storage technology	[-]
CCD	Computational Combustion Dynamics	[-]
CSTR	continuously stirred tank reactor	[-]
2D	two dimensional	[-]
3D	three dimensional	[-]
D_v	the diffusion coefficient of oxygen vacancies through the membrane	$[m^2/s]$
Dkk model	D_v , k_f and k_r coefficients oxygen permeation model	[-]
DO	Discrete ordinates	[-]
$D_{i,m}$	Diffusion coefficient for species	$[m^2/s]$
EOP	electro-chemical oxygen pumps	[-]
F	Feed channel	[-]
IGCC	Integrated gasification combined cycle	[-]
HTM-ASU	high temperature membrane air separation unit	[-]
ITM	Ion Transport Membranes	[-]
J_{O_2}	Oxygen permeation flux	$[mol/s]$
κ	Absorption coefficient	$[1/m]$
k_f	The forward reaction rate constant for the surface exchange reaction on the membrane surface	$[m/atm^{0.5}.s]$
k_r	The reverse reaction rate constant for the surface exchange reaction on the membrane surface	$[mol/m^2.s]$
L	Normal distance between membrane surface and sweep gas inlet	$[m]$
LES	large-eddy simulation	[-]
LSCF	lanthanum strontium cobaltite ferrite	[-]
LSCF-1991	$La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$	[-]
MEA	methylethanolamine	[-]
NGCC	Natural gas combined cycle	[-]
NO_x	Nitric oxides	[-]
OCM	oxidative coupling of methane	[-]
OTM	Oxygen Transport Membranes	[-]
P	Permeate channel	[-]
PC	Pulverized coal power plant	[-]
PCC	post-combustion capture	[-]
PF	pulverized fuel	[-]
P'_{O_2}	oxygen partial pressure at feed side	$[Pa]$
P''_{O_2}	oxygen partial pressure at permeate side	$[Pa]$
PSA	pressure swing adsorption	[-]

P_{tot}	Total pressure	[bar]
RANS	Reynolds-averaged Naviere-Stokes	[-]
RFG	recycled flue gas	[-]
R_1	Mass rate of creation or depletion	[kg/s]
RNG	Renormalized group	[-]
RTE	Radiative transfer equation	[-]
S	source/sink term	[m ³ /s]
sccm	Standard cubic centimeter per minute.	[-]
Sc_t	Turbulent Schmidt number	[-]
SOFC	solid oxide fuel cells	[-]
T_{in}	Inlet temperature	[°C]
u_j	Velocity component	[m/s]
V_C	the computational cell volume	[m ³]
Y	The distance through the symmetry line starting from the origin	[m]
YSZ	Yttria-stabilized zirconia	[-]
ZEPP	Zero emission power plant	[-]

Greek symbols

Φ	Equivalence ratio	[-]
Γ_Φ	Diffusion coefficient	[m ² /s]
$\bar{\rho}$	Fluid density	[kg/m ³]
c_μ	Constant	[-]
$e_{b\lambda}$	Blackbody spectral emissive power	[W]
μ_t	Turbulent viscosity	[kg/m.s]
σ_Φ	Constant	[-]
σ_s	Scattering coefficient	[-]
σ_V	oxygen vacancy conductivity	[-]
ε	Epsilon	[-]

Subscripts

avg	Average
exp	experimental
f	fuel
feed	Feed side of membrane
mem	Membrane
Num	numerical
sweep	Sweep side of membrane

Superscripts

°	Rate
o	Degree

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VITA



Dr. Medhat A. Nemitallah was born in Kafr-Elshiekh, Egypt. He received his bachelor's degree in 2006 with GPA of 89.92% with degree of honor from Alexandria University. He was the 2nd in a batch of more than 600 students. Also, he received his Master degree in 2009 from the same university. He worked as a demonstrator at Alexandria University from 2007 to 2010. He joined KFUPM University, Saudi Arabia, in 2010 and worked as Lecture B till 2013. He finished his PhD program in less than three years with full GPA of 4/4 in all of the courses.

2010-present Dr. Nemitallah joined the PhD program in the Mechanical Engineering Department at KFUPM University, Saudi Arabia, in September, 2010. He worked as lecturer B in the department and he taught different courses like ME316 and PHY102. He has finished his PhD program courses with full GPA of 4 out of 4. During his PhD program, he participated in many research projects with his advisor and MIT group and other professors in the department. During his program, he produced one patent and 12 high rank journal papers, in addition to 7 conference papers. He completed his PhD program at KFUPM University under mixed supervision between KFUPM and MIT universities in less than three years, in March 2013.

2007-2010 As he was the 2nd in a group of more than 600 students for four years in Mechanical engineering department at Alexandria University, he was accepted to work as a demonstrator during this period. He taught many courses in this period in the field of combustion and gas dynamics. He finished his master courses with a GPA of almost 4 out of 4. He has also produced four journal papers out of his master thesis work. He finished his M.Sc. thesis in two years then, he got the teaching assistant degree in 2009 at Alexandria University.

2001-2006 He joined the Faculty of Engineering at Alexandria University, Egypt. He got his B.Sc. degree in Mechanical Engineering in 2006 with GPA of 88.92 % with degree of Honour. He was the 2nd in a patch of more than 600 students. The grade for the final year and final year project was distinction 92.6 % and 100 %, respectively.

TEACHING EXPERIENCE

- Automotive Engineering, Gas dynamics, Internal combustion Engines, Part I, II and labs courses in Mechanical Engineering Department for junior and senior class from 2007 to 2010, at Alexandria University.
- Thermo-fluid labs in Mechanical Engineering Department and General Physics courses in Physics Department for junior and senior class at KFUPM, 2010-2013.

WORK EXPERIENCE

- Demonstrator, in Mechanical Engineering Department from 2007 to 2010 at Faculty of Engineering at Alexandria University, Alexandria, Egypt.
- Lecturer B in Mechanical Engineering Department at KFUPM University, Dhahran, Saudi Arabia.

SKILLS

- ✓ **Computing:** FORTRAN, Matlab, and Visual C++ programming languages. Technical CFD packages including ISIS, FLUENT, ANSYS and KIVA (CFD codes).
- ✓ **Languages:** Excellent communication skills in both English and Arabic languages.

PROFESSIONAL QUALIFICATIONS

- Member of the Egyptian Engineers Syndicate.
- Member of Alexandria University Faculty-Corporation, Alexandria, Egypt.

AREAS OF INTEREST

- He is so excited to work in Hydrogen, Natural gas or Bio-diesel fuels as alternative new fuels for combustion.
- He has experience in external and internal combustion research using both experimental and numerical approaches and he can work in the thermo-fluids field research.
- He has experience in designing setting up boilers and gas turbine.