Investigation into the Possible Use of an Oxygen Ion Transport Membrane Combustion Unit in an Oxyfired Power Plant

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Investigation into the Possible Use of an Oxygen Ion Transport Membrane Combustion Unit in an Oxyfired Power Plant

Kirsten Foy

PhD

Dublin Institute of Technology

2007
Investigation into the Possible Use of an Oxygen Ion Transport Membrane Combustion Unit in an Oxyfired Power Plant

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Dublin Institute of Technology
Supervisor: Professor Jim McGovern
School of Mechanical and Transport Engineering

September 2007
Abstract

It is generally recognised that carbon dioxide (CO₂) emissions damage the environment. Carbon capture and storage offers the possibility of using fossil fuels for power production without releasing CO₂. In the proposed ZEITMOP power plant cycle hydrocarbon fuel is burned in a mixture of oxygen and CO₂, allowing easy separation of combustion products to capture the CO₂ for sequestration. Oxygen ion transport membranes (OTMs) provide oxygen. The original configuration of the cycle requires an OTM air separation unit, in which oxygen is separated from air and mixed with CO₂, and a separate combustion chamber, in which fuel is burned in this mixture.

Another possibility is to use a combined OTM combustion chamber and air separation unit. The oxygen is consumed by the combustion as soon as it permeates through the OTM, and the operating temperature of the OTM unit is the combustion temperature. The aim of the current research is to investigate the possible use of an oxygen ion transport membrane combustion unit in the ZEITMOP oxyfired cycle.

OTM materials were compared. The combined ZEITMOP cycle was simulated. During the course of the research a new cycle was developed and named the OFFCET cycle. The results of initial calculations on this cycle are described. An experimental rig was designed and built. Some work was also carried out on the ZEMPES cycle.

It was found that the efficiency of the combined cycle using a perovskite unit would be very low due to the low operating temperature. The efficiency of the combined cycle with a fluorite unit may be higher than the efficiency of the separate cycle at the same combustion temperature. A fluorite OTM combustion unit operating at 1400°C would be of a similar size to a perovskite OTM air separation unit operating at 875°C.
Declaration

I certify that this thesis which I now submit for examination for the award of PhD, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award in any other Institute or University.

The work reported on in this thesis conforms to the principles and requirements of the Institute's guidelines for ethics in research.

The Institute has permission to keep, to lend or to copy this thesis in whole or in part, on condition that any such use of the material of the thesis be duly acknowledged.

Signature _____________________________  Date ____________

Candidate
Acknowledgements

I would like to thank my mother Martha for all her help.

Thanks also to my supervisor Professor Jim McGovern.

For help with the rig: Dean, Ken, Paul and Colm.

For help with the microscope: Dr. Des.

For support and encouragement: Eoin Plant and Barry Haycock.

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DIT provided extra funding for equipment.
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<td>Ar</td>
<td>Argon</td>
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<tr>
<td>AZEP</td>
<td>Advanced Zero Emission Power</td>
</tr>
<tr>
<td>CAR</td>
<td>Ceramic Autothermal Recovery</td>
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<tr>
<td>CES</td>
<td>Clean Energy Systems</td>
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<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
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<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
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<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>ECBM</td>
<td>Enhanced Coal Bed Methane recovery</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced Oil Recovery</td>
</tr>
<tr>
<td>H₂O</td>
<td>Steam/Water Vapour</td>
</tr>
<tr>
<td>H₂O (l)</td>
<td>Liquid Water</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
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<tr>
<td>O₂</td>
<td>Oxygen</td>
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<tr>
<td>OCDOPUS</td>
<td>Oil enhancement Carbon Dioxide Oxygen Power Universal Supply</td>
</tr>
<tr>
<td>OFFCET</td>
<td>Oxygen Fired Fuel Cell Energy Turbine</td>
</tr>
<tr>
<td>OFFCSET</td>
<td>Oxygen Fired Fuel Cell Steam Energy Turbine</td>
</tr>
<tr>
<td>OTM</td>
<td>Oxygen ion Transport Membrane</td>
</tr>
<tr>
<td>slpm</td>
<td>Standard Litres Per Minute</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
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<tr>
<td>YSZ</td>
<td>Yttria Stabilised Zirconia</td>
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<tr>
<td>ZEMPES</td>
<td>Zero Emissions Membrane Piston Engine System</td>
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<td>ZENG</td>
<td>Zero Emission Norwegian Gas</td>
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<td>BaBi$<em>{0.4}$Co$</em>{0.2}$Fe$<em>{0.4}$O$</em>{3-d}$</td>
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<tr>
<td>BCF</td>
<td>BaCe$<em>{0.15}$Fe$</em>{0.85}$O$_{3-d}$</td>
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<tr>
<td>BSCF</td>
<td>Ba$<em>0.5$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-d}$</td>
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<tr>
<td>BTFC</td>
<td>BaTi$<em>{0.2}$Co$</em>{0.5}$Fe$<em>{0.3}$O$</em>{3-d}$</td>
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<td>CLFC</td>
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<td>CP</td>
<td>Ce$<em>{0.7}$Pr$</em>{0.3}$O$_{2-d}$</td>
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<tr>
<td>CPZ</td>
<td>Ce$<em>{0.7}$Pr$</em>{0.2}$Zr$<em>{0.1}$O$</em>{2-d}$</td>
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<td>LCF</td>
<td>La$<em>{0.4}$Ca$</em>{0.6}$FeO$_{3-d}$</td>
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<td>LCFC</td>
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<tr>
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<td>LSCF</td>
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<td>LSCF fibre</td>
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<td>LSGF</td>
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<td>LSGF-BSCF</td>
<td>12.8La$<em>{0.15}$Sr$</em>{0.85}$Ga$<em>{0.3}$Fe$</em>{0.7}$O$<em>{3-d}$ Ba$</em>{0.5}$Sr$<em>{0.5}$Fe$</em>{0.2}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-d}$</td>
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<td>SCN</td>
<td>SrCo$<em>{0.9}$Nb$</em>{0.1}$O$_{3-d}$</td>
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<td>SCT</td>
<td>SrCo$<em>{0.85}$Ti$</em>{0.15}$O$_{3-d}$</td>
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<td>SLFC</td>
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<td>SLFCC</td>
<td>Sr$<em>{0.8}$La$</em>{0.2}$Fe$<em>{0.7}$Cr$</em>{0.2}$Co$<em>{0.1}$O$</em>{3-d}$</td>
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<td>SLFT</td>
<td>Sr$<em>{0.8}$La$</em>{0.2}$Fe$<em>{0.8}$Ti$</em>{0.2}$O$_{3-d}$</td>
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<tr>
<td>ZTY</td>
<td>0.8ZrO$_2$0.1TiO$_2$0.1Y$_2$O$_3$</td>
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<td>160</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
<td>C/mol</td>
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<tr>
<td>$j_{O_2}$</td>
<td>Oxygen flux</td>
<td>mol/m$^2$/s</td>
</tr>
<tr>
<td>$L$</td>
<td>Membrane thickness</td>
<td>m</td>
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<tr>
<td>$m$</td>
<td>Mass flow rate</td>
<td>kg/s</td>
</tr>
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<td>$n$</td>
<td>Charge on charge carrier (= 2 for Oxygen ions)</td>
<td></td>
</tr>
<tr>
<td>$P_1$</td>
<td>Oxygen partial pressure at feed side</td>
<td>Pa</td>
</tr>
<tr>
<td></td>
<td>Pressure at start of process</td>
<td>Pa</td>
</tr>
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<td>$P_2$</td>
<td>Oxygen partial pressure at permeate side</td>
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<td>$P_{O_2,c}$</td>
<td>Oxygen Partial Pressure at the Cathode (Air Side)</td>
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<td>$P_{O_2,a}$</td>
<td>Oxygen Partial Pressure at the Anode (Fuel Side)</td>
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<td>$q$</td>
<td>Specific heat transfer</td>
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<td>$R$</td>
<td>Ideal gas constant</td>
<td>J/molK</td>
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<td>Temperature</td>
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<td>Average temperature</td>
<td>K, °C</td>
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<td>$V$</td>
<td>Voltage or Potential</td>
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<td>$w$</td>
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<td>--------</td>
<td>------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>γ</td>
<td>Ratio of specific heats</td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>Specific exergy</td>
<td>J/kg</td>
</tr>
<tr>
<td>σᵢ</td>
<td>Material conductivity</td>
<td>S/m</td>
</tr>
<tr>
<td>μ</td>
<td>micro (= 10⁻⁶)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Specific chemical exergy</td>
<td>J/kg</td>
</tr>
<tr>
<td>η</td>
<td>Exergetic efficiency</td>
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1. Introduction

Climate change is becoming more noticeable and public awareness of the problem has grown. The majority of the public and most governments now accept the fact that climate change is a reality. The best evidence suggests that the change in climate has been caused at least partly by human activity. Global warming can no longer be denied; it is a fact that the average temperature of the earth is now higher than it was at the time of the industrial revolution. Eleven of the last twelve years (1995 – 2006) rank among the twelve warmest years in the instrumental record of global surface temperature (since 1850). The area of the Arctic icecap has shrunk by about 3% per decade since 1978 and mountain glaciers and snow cover have declined on average all over the Earth.

Perhaps more worryingly, simulation of the effects of a CO$_2$-induced increase in temperature of only 0.8°C – 2.4°C in hurricane storm basins suggests that while the total number of hurricanes would not be increased, the number of level 5 hurricanes would significantly increase. Emanuel reports that “the large upswing [in hurricane intensity] in the last decade is unprecedented, and probably reflects the effect of global warming.” The hurricane season in Florida in 2005 was a stark indication of what the future could hold unless global warming is halted.

In addition to this, it has long been predicted that the change in temperature of the oceans could affect global ocean currents. The Intergovernmental Panel on Climate Change reported that “based on current model simulations, it is very likely [likelihood higher than 90%] that the meridional overturning circulation (MOC) of the Atlantic Ocean [the system of currents including the North Atlantic Drift] will slow down during the 21st century.” As Ireland relies on the North Atlantic Drift for its mild
weather, this implies that global warming will most likely reduce the temperature in Ireland in addition to increasing precipitation.

It is now generally accepted that the increase in the temperature of the earth is linked to the increase in greenhouse gases, mostly CO$_2$, in the atmosphere. Ireland has ratified the Kyoto protocol, which sets strict limits on emissions of CO$_2$ and imposes penalties. Ireland’s allowed emissions under the Kyoto protocol are 63 Mt CO$_2$eq per year for the years 2008 – 2012$^5$. Ireland’s emissions in 2005 were 70 Mt CO$_2$eq.$^5$ It is projected that Ireland will miss this target and the Irish government has allocated financial resources to use Kyoto mechanisms.$^6$ These mechanisms allow industrialised countries to invest in emissions-savings projects in other countries and use the resulting emission credits to help meet their Kyoto targets. However it is projected that even with these measures Ireland will still miss the target and will face major fines under the Kyoto protocol or will have to purchase carbon credits from 2008 onwards.$^6$ If greenhouse gas emissions are not drastically reduced by 2012 the penalties will become more severe.

CO$_2$ is a major greenhouse gas released whenever fuels containing carbon, such as methane, are burned. Most of our heating, transport and energy needs are met by combustion of hydrocarbon fuels. Renewable energies are carbon neutral and so present a favourable solution to the problem of greenhouse gas emissions. Unfortunately renewable energy technologies are currently underdeveloped in comparison to fossil fuel based technologies. Much work is required before such energy sources will produce a major portion of our energy. Nuclear power is another method of power production that does not contribute to the global warming problem. However acceptance of nuclear power by the public is quite low, particularly in Ireland.
Fossil fuels are well understood by the power industry, and are still relatively cheap and abundant. The Hubbert oil peak is the maximum production of oil. In theory it coincides with the midpoint of the available oil in a region. Various current estimates place the world peak between 2009 and 2035\(^7\), implying that there is at least as much oil still available in the world as has been consumed since the industrial revolution. With the discovery of methane hydrates it appears that there are vast quantities of methane in the world\(^8\). It is inevitable that fossil fuel will continue to be used for decades to come. Unfortunately combustion of these fuels produces CO\(_2\), the main contributor to global warming. One challenge facing engineers is how to reduce or prevent the negative impact on the climate caused by CO\(_2\) emissions from power plants, while allowing the continued use of fossil fuels for power production.

Carbon capture and storage means capturing CO\(_2\) and trapping it away from the atmosphere, which is also called carbon sequestration. There are many methods of sequestering CO\(_2\). The most advanced is Enhanced Oil Recovery (EOR), which involves injecting CO\(_2\) into partially depleted oil wells to increase the pressure and produce more oil. This is currently common practice in many oil companies. Over 7 Mt of CO\(_2\) have been injected into one oil well in Canada and no adverse effects have been documented\(^9\). Enhanced Coal Bed Methane Recovery (ECBM) is also a well developed method of harvesting methane from unmineable coal by injecting CO\(_2\) into the coal bed. At present CO\(_2\) is purchased for these purposes. Fully depleted oil wells could also be used for long term CO\(_2\) storage. CO\(_2\) can be used to neutralize alkali pollutants in polluted areas. It can also be dissolved in the deep sea, although there are localised adverse effects. Yet another method is to absorb CO\(_2\) into coal beds that are inaccessible and cannot be mined. Some minerals will react with CO\(_2\) to form a solid
product. There are two methods of doing this – mining the reactant mineral and reacting it with CO\(_2\) to produce a product which can be used in road building, or injecting CO\(_2\) into subterranean caverns containing the reactant mineral, and allowing it to slowly react over time. Other methods of CO\(_2\) storage include injection into some geological formations, particularly porous rock. It is possible to calculate in advance the storage capacity of various types of geological formation. Akinfiev et al.\(^10\) present theoretical calculations for formation of methane by a reaction of CO\(_2\) with fayalite, an abundant mineral, and discuss the possibility of a closed carbon cycle. In effect, fayalite becomes a fuel, with methane being the energy carrier, and no emissions to atmosphere. Many studies are being undertaken on sequestration, and many numerical simulations have been developed and tested.\(^{11,12}\)

There are many methods of capturing CO\(_2\) produced by combustion of fossil fuels for production of electricity. The fuel may be burned in air, and the exhaust products separated to capture the CO\(_2\). This usually involves either cryogenic or chemical processes, or use of membranes to separate gases. It is very difficult to remove 100\% of CO\(_2\) from the mixture of combustion product gases. Alternatively, carbon may be removed from hydrocarbon fuel before combustion, for example by conversion of methane to syngas, a mixture of carbon monoxide (CO) and hydrogen (H\(_2\)), followed by separation of H\(_2\) from the mixture. It is possible to produce very pure H\(_2\) by this method, so that the H\(_2\)-using technology is emission free. However it is difficult to separate CO from H\(_2\) as both are gases and the remaining CO will contain some unseparated H\(_2\). This mixture is also an energy rich fuel source, and CO\(_2\) will be produced by burning this CO-rich syngas.
Oxyfiring technology, also called oxycombustion, oxyfuel or zero emissions technology, is a method of carbon capture that enables 100% of CO₂ to be captured. Although there is only one oxycombustion plant in operation today, there are many possible cycles in development. There are many technologies utilising oxyfiring of fossil fuels, not all of which involve power production.¹³

Oxyfiring involves burning a hydrocarbon fuel in pure oxygen (O₂) rather than in air. The combustion products contain only CO₂ and water vapour (H₂O). As combustion in pure oxygen results in extremely high temperatures, the temperature can be reduced by burning in a mixture of O₂ and CO₂ and/or H₂O. After useful energy is extracted, the water is condensed out, leaving an almost pure stream of CO₂, which may be compressed to a very high pressure for sequestration or further use. Some of the fluid may recirculate to be mixed with oxygen and return to the combustion chamber. No CO₂ is released into the atmosphere. In fact, no emissions of any kind are released: the water also leaves the plant as liquid, hence it is an effluent not an emission, although it may require some cleaning.

Any impurities (e.g. sulphur dioxide) or incompletely burned products (e.g. CO) are not pollutants, but rather dissolved impurities in the CO₂. As the fuel is not burned in the presence of nitrogen, there are no noxious gases in the products, or in the air which returns to the atmosphere. Oxyfired power plants offer the possibility of producing energy from hydrocarbon fuels without contributing to the increase in CO₂ in the atmosphere.

Such proposed power plants are currently not as efficient as existing power plants. The CO₂ must be compressed for transportation to the sequestration site, using some of the power produced by the plant. The oxygen required for combustion must be separated from the air. Mature oxygen production technologies, such as cryogenic
separation, are energy intensive and so the overall efficiency of the power plant is reduced.

Oxygen ion transport membranes (OTMs) are dense ceramic membranes which allow oxygen and only oxygen to pass through the membrane. They have been the subject of much research in the past decade, and new materials are continually being created. They could be used to create a mixture of O₂ and another gas, e.g. CO₂, if air were on the feed side of the membrane and CO₂ on the permeate side. Alternatively, air could pass over the feed side, a mixture of fuel and CO₂ could pass over the permeate side, and combustion could take place in a chamber made of the ceramic. There are two main types of OTMs: perovskite and fluorite. Perovskite membranes generally have a higher overall rate of oxygen flow through the membrane (oxygen flux) than fluorite membranes, but have a lower maximum operating temperature.

The Zero Emissions Ion Transport Membrane Oxygen Power (ZEITMOP) cycle is a theoretical oxyfired power plant cycle which uses OTMs to produce the required oxygen. The original cycle uses an OTM unit to separate O₂ from air and mix it with CO₂. Methane is then burned in this mixture in a separate combustion chamber. This configuration of the cycle is referred to in this thesis as ZEITMOP-Separate. A second possibility is to burn methane in an OTM unit, in which compressed air provides oxygen to the feed side of the membrane and the oxygen is consumed by the combustion reaction on the permeate side of the membrane. The configuration of the ZEITMOP cycle incorporating this combined OTM combustion unit is referred to in this thesis as ZEITMOP-Combined. The aim of the current research is to investigate the technological considerations surrounding the use of an
A literature review was undertaken to provide a context for the current research. This is described in Chapter 2 of this thesis. Oxyfired cycles and OTMs were reviewed in detail and the previous work on the ZEITMOP cycle is described. Some groups have developed and tested OTM units designed for use in oxyfired plants. The available literature on these units is also presented. The available literature on OTMs was compiled and a detailed comparison of the available materials was carried out and is presented in Chapter 3 of this thesis. This provided information on the type of membranes most likely to be used in either the ZEITMOP-Separate plant (perovskites) or the ZEITMOP-Combined plant (fluorites). It was also possible to estimate expected oxygen fluxes for the conditions that would occur in a ZEITMOP plant.

Chapter 4 describes the methodology followed during the current research. The OFFCET cycle and the work carried out on the development of the ZEMPES cycle are also presented here.

Initial calculations were performed using Microsoft Excel on the ZEITMOP-Separate cycle and the ZEITMOP-Combined cycle. These calculations implied that the ZEITMOP-Combined cycle would have a similar efficiency to the ZEITMOP-separate. A different power plant design, OFFCET, was developed and initial Excel calculations were also performed on it. These showed that the efficiency of the OFFCET cycle compared favourably with that of the ZEITMOP cycle.

The ZEITMOP-Combined cycle was simulated using AspenPlus, with a simplified OTM model that uses standard AspenPlus modules. This OTM model is
described in Section 5.2.2 and is similar to, but slightly more accurate than, the model used by a previous researcher to simulate the ZEITMOP-Separate cycle. The results of these simulations were analysed and compared to previous work on the ZEITMOP-Separate cycle. A new model for the OTM unit, described in Section 5.2.3, was developed based on the actual physical processes in the OTM combustion unit. This new model performed as well as the previous model and the ZEITMOP-Combined cycle was simulated with and without heat transfer from the air stream to the CO₂ stream using AspenPlus, with the new OTM model. All the calculations and simulations are presented in Chapter 5 of this thesis, and the results are presented in Chapter 7.

An experimental rig was designed and built during the course of the research. The work carried out is described in Chapter 6 and the results of the tests performed are presented in Chapter 7. Chapter 8 presents the conclusions of the research.
2. Literature Review

2.1. Oxyfired Power Plants

Many oxyfired thermodynamic cycles have been invented and simulated. A number of oxyfired power plant designs have been developed to the extent of machinery design. Some have reached laboratory scale, with tests on physical prototypes of units designed for the oxyfired cycle. In March 2005 the world’s first oxyfired power plant, created by Clean Energy Systems (CES), began producing power in Kimberlina, California, U.S.A.\textsuperscript{16}

The compression of CO\textsubscript{2} reduces the efficiency of the plant, but the reduction may be acceptable given the damaging effects of CO\textsubscript{2} emissions. Production of oxygen further reduces the efficiency. The most mature method of oxygen production is cryogenics, an energy intensive process involving freezing air. OTMs potentially offer a much more efficient method of producing oxygen, with the result that many oxyfired plant cycles incorporate these membranes.

Sections 2.2 and 2.4 present the previously published work on the most relevant cycles to the current research. All values given for efficiencies of previously published oxyfired cycles are taken from the referenced papers and were calculated using different assumptions, models and boundary conditions. These sections are not a comparative evaluation of the different cycles and the values given should be considered as a guide only.

2.2. Oxyfired Cycles that do Not use OTMs

In 1996 CES patented a cycle in which fuel, pure oxygen and water enter a combustor based on rocket engine technology.\textsuperscript{17} This combustor, designed by aerospace engineers, produces a very hot (~1650 °C) jet of 90% steam (H\textsubscript{2}O) with
10% CO₂. This jet must be cooled before it can enter currently available turbines. A number of removable sections inject more water to cool and increase the mass flow rate of the jet. As turbine technology improves, these stages may be removed, increasing the turbine inlet temperature and allowing the plant to increase in efficiency. The turbine exhaust is cooled in stages, condensing out the water for recirculation. Some of the water is waste; the majority is recirculated to the jet. The CO₂ is compressed for sequestration.¹⁸ The O₂ is produced by an unspecified air separator, which may be cryogenic or OTM based. The CES cycle is shown in Figure 1.

N₂ = Oxygen-depleted air, HP = High Pressure, RH = Reheater, IP = Intermediate Pressure, LP = Low Pressure, HX = Heat Exchanger, Cond. = Condenser, CW = Cooling Water, NG = natural gas
A demonstration plant in Kimberlina, California, began operation in February 2005. The plant is a staged retrofit of an existing power plant. The O₂ is currently produced externally, but an onsite air separation plant is planned. Currently the CO₂ is emitted to atmosphere, but in the completed system it will be compressed onsite and sequestered. The purity of the CO₂ stream produced was about 95%. A combustor producing 20 MW of thermal energy has been successfully tested, although the cycle efficiency of this demonstration plant is limited because the turbine capacity is only 5.5 MW. The Kimberlina plant is the first oxyfired power plant in the world. This plant, always intended to be a demonstration plant rather than a commercial enterprise, will soon be joined by a 40 MW plant in Holland and a commercial 50 MW plant in Norway. In recent years an improved cycle has been developed, in which the oxygen-depleted air from the air separator is used to provide power. This new scheme, shown in Figure 2, is called the Zero Emissions Norwegian Gas (ZENG) Project.

![Figure 2: The ZENG Project Cycle](image-url)
ASU = Air Separation Unit, HP = High Pressure, LP = Low pressure, GG = Gas Generator, RH = Reheater, TX = turbine Expander, IP = Intermediate Pressure, LHV = Lower Heating Value

The air is compressed in the ASU and a portion of the depleted air (referred to as Nitrogen in the diagram) is heated by the combustion gases and expanded to produce work. This has the effect of adding a bottoming Joule cycle (gas turbine cycle, also called a Brayton cycle, a description of which can be found in most thermodynamic textbooks) and offers a significant benefit. The thermodynamic efficiency of the ZENG cycle is 45% as shown in Table 1.

<table>
<thead>
<tr>
<th>“Optimised” Cycle Summary Data</th>
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<tbody>
<tr>
<td>Thermal power input</td>
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<tr>
<td>Gross power output</td>
<td>58.6 MWe</td>
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<tr>
<td>Parasitic power</td>
<td>8.1 MWe</td>
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<tr>
<td>Net power</td>
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<tr>
<td>Overall cycle efficiency</td>
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<td>Fuel consumption</td>
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<td>Oxygen consumption</td>
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<td>Cooling water flow (total)</td>
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<td>150 bar</td>
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<td>HP Turbine inlet temperature</td>
<td>600 °C</td>
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<tr>
<td>HP Turbine exhaust temperature</td>
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<td>IP Turbine inlet pressure</td>
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<td>IP Turbine inlet temperature</td>
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<tr>
<td>IP Turbine exhaust temperature</td>
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<tr>
<td>CO2 / Steam Condenser pressure</td>
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<table>
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<tr>
<td>LP Turbine inlet temperature</td>
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<td>LP Turbine exhaust temperature</td>
<td>24 °C</td>
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<tr>
<td>Steam Condenser pressure</td>
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</table>

Table 1: Technical Data for the ZENG Project Cycle²⁰
The Graz cycle was first introduced in 1995\textsuperscript{21} and has been continually developed. It is similar to the CES cycle in that $\text{H}_2\text{O}$ is recirculated to the combustion chamber, however it is more complex than the CES cycle. The cycle has also been developed for a coal-derived syngas plant.\textsuperscript{22}

In the original cycle, shown in Figure 3, the combustion products (80\% $\text{H}_2\text{O}$ and 20\% $\text{CO}_2$) power a high temperature turbine, after which about half is cooled, compressed and re-enters the combustion chamber, while the rest enters an intermediate pressure turbine. After the intermediate stage, a portion is bled off and the water condensed out. The rest enters a low pressure turbine and is then cooled, with the water condensed out. The $\text{CO}_2$ is captured at the pressure of the intermediate turbine (atmospheric pressure). The water captured at low pressure is pumped to a very high pressure and heated. It then enters a steam turbine before returning to the combustion chamber. An efficiency of 56.8\% of higher heating value was claimed for this cycle, however the cycle assumes a supply of pure $\text{O}_2$, and the $\text{CO}_2$ is provided at atmospheric pressure.
The Graz cycle has been developed in a practical manner, making use of the expertise available within the Institute of Thermal Turbomachinery and Machine Dynamics at Graz University of Technology in Austria in gas and steam turbine and heat exchanger design. This development led to a majority CO₂ flow cycle, which led to a significant body of work on the development of a majority (77% by mass) CO₂ turbine. However, further development returned to a majority steam cycle (62% at turbine inlet) fuelled by syngas, for which an efficiency of 70% was claimed, falling to 58% when O₂ production and liquefaction of CO₂ was taken into account. Based on these results, Statoil became interested in the project and initiated an investigation into
the Graz cycle. This resulted in a realistic efficiency of 52.6% for a natural gas fired cycle, shown in Figure 4, with 74% H\textsubscript{2}O at turbine inlet, which takes into account not only O\textsubscript{2} supply and compression of CO\textsubscript{2} to 100 bar, but also mechanical, electrical and auxiliary losses.\textsuperscript{25} Ignoring these last 3 losses, the efficiency would be 54.6%. The production of O\textsubscript{2} reduced the efficiency by 9.8 percentage points. The compression of CO\textsubscript{2} reduced the efficiency by a further 2.2 percentage points.

![Figure 4: The Current Graz Cycle\textsuperscript{25}](image)

HTT = High Temperature Turbine, C = Compressor, HPT = High Pressure Turbine, HRSG = Heat Recovery Steam Generator, LPT = Low Pressure Turbine, Cond. P. = Condensing Pressure

The Oil Enhancement Carbon Dioxide Oxygen Power Universal Supply (OCDOPUS)\textsuperscript{26} cycle concept shown in Figure 5 is an oxyfired cycle integrated with EOR. Use of both the CO\textsubscript{2} and depleted air produced is considered for EOR. Holt and
Lindeberg\textsuperscript{27} claimed in 1992 that two thirds of the CO\textsubscript{2} produced by combustion of Earth’s oil and gas reserves could be stored in Earth’s oil and gas reservoirs.

![Figure 5: The OCDOPUS Cycle Concept\textsuperscript{26}](image)

**2.3. Oxygen Ion Transport Membranes**

Oxygen Ion Transport Membranes (OTMs) are solid ceramic membranes which contain oxygen ion vacancies in the molecular lattice. When excited, e.g. when heated, oxygen ions can travel through the ceramic. O\textsubscript{2} molecules are adsorbed onto the surface and separate into O\textsuperscript{2-} ions, taking electrons from the ceramic to do so. The oxygen ions can travel equally well in both directions, with the result that when there is a higher oxygen partial pressure on one side of a membrane than the other, oxygen will pass through from the oxygen-rich side to the oxygen-lean side. The ions then reform as molecules on the other side of the membrane, releasing their electrons back into the ceramic. The electrons are conducted back through the membrane to the
higher oxygen side. The overall effect is that oxygen and no other gas can travel through the membrane. The Nernst-Einstein equation, Equation 1, describes how the oxygen flux is affected by various parameters.

\[
J_{O_2} = \frac{\sigma_i R T}{4 L n^2 F^2} \ln \left( \frac{P_1}{P_2} \right)
\]

- \(F\)  
  Faraday’s constant
- \(J_{O_2}\)  
  Oxygen flux
- \(L\)  
  Membrane thickness
- \(n\)  
  Charge on charge carrier (= 2 for Oxygen ions)
- \(P_1\)  
  Oxygen partial pressure at feed side
- \(P_2\)  
  Oxygen partial pressure at permeate side
- \(R\)  
  Ideal gas constant
- \(T\)  
  Temperature
- \(\sigma_i\)  
  Material conductivity

Equation 1: The Nernst-Einstein Equation\textsuperscript{14}

The driving force behind the oxygen transport is the difference in partial pressures across the membrane. While the membrane itself does not use power or work, energy is required to produce this difference in partial pressures. For example, to produce oxygen at atmospheric pressure, air must be compressed to at least 4.76 atm and introduced to one side of the membrane. As the ions must also be excited, energy is also required to heat the air and membrane to the temperature required for the
membrane to operate as an OTM. The transfer of ions and electrons through the membrane is an electrical conduction process, so any energy losses will be converted into heat in the membrane. Energy is also required to draw the oxygen away from the membrane.

Although the effect has been known for many years, it was not until 1985, when Teraoka et al.\textsuperscript{28} discovered exceptionally high oxygen flux through perovskite ceramics, that engineering interest in OTMs really began. Some research has been conducted into the use of OTMs to produce pure oxygen.\textsuperscript{29} This results in an oxygen stream which has a total pressure less than the partial pressure of oxygen in the feed gas. For example, to produce pure oxygen at 10 bar on the permeate side of the membrane, air at more than 47.6 bar must be present on the feed side of the membrane. This total pressure difference puts heavy demands on the physical strength of the membrane.

Much research has been conducted into the use of OTMs to produce a mixture of oxygen and another gas. In this manner the total pressure difference across the membrane can be reduced or eliminated. This is the configuration required in the ZEITMOP-Separate cycle.

A third use for OTMs has also been identified. Methane is more abundant than oil; however a number of methane fields are in remote locations. The methane would be more accessible if it were converted to liquid. One step in this process is the catalytic partial oxidation of methane to synthesis gas, or syngas. Syngas is a mixture of CO and H\textsubscript{2}, and can be formed by a reaction between O\textsubscript{2} and methane in the presence of a catalyst. OTM tubes can be packed with this catalyst (or a plate can be coated with it). Therefore there has also been a substantial amount of research on
OTMs used to convert methane to syngas, an exothermic reaction that uses up oxygen. If methane flows on the catalyst-containing side, the oxygen that passes through will be quickly used up in the reaction. This causes a continually low oxygen pressure on the permeate side, and so greatly increases the oxygen flux.\textsuperscript{30} When used in this way, the flux across a tubular membrane can be up to 8 times the oxygen flux when used to oxygenate a sweep gas.\textsuperscript{30}

Research has also been conducted using a mixture of CO\textsubscript{2} and CO on the permeate side of the membrane. This research clearly demonstrated that the flux through the membrane was significantly higher when the CO was being oxidised (i.e. when the O\textsubscript{2} was being consumed) than when there was no CO left to oxidise.\textsuperscript{31} It seems likely that using an OTM for combustion, i.e. burning a fuel in an OTM tube, using oxygen passing through the membrane, would provide a high flux. This is the configuration required in ZEITMOP-Combined. Praxair, a leading ceramic manufacturer, have developed membranes specifically for this method of combustion, and have demonstrated the feasibility of this process, but have not released details of the oxygen fluxes achieved.\textsuperscript{32,33}

Most membrane materials are only conductive to O\textsubscript{2} above 700°C (975 K)\textsuperscript{35}. Above this temperature the flux is proportional to the temperature, so an exothermic oxygen-consuming reaction on the permeate side of the membrane should provide a high flux. Combustion seems ideal. However, at very high temperatures the ceramic lattice will sinter\textsuperscript{34} (become denser), irreversibly changing the properties of the OTM, and at higher temperatures it will melt.

There are three main types of ceramics with ion transport capabilities: perovskite, fluorite and mixed. Perovskite ion transport ceramics have the chemical
structure ABO$_3$. There may be a mixture of 2 or more elements in the A-site and/or the B-site, e.g. Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-d}$ (BSCF). Fluorite ion transport ceramics have the structure AO$_2$ and again there may be two or more elements in the A-site e.g., Ce$_{0.7}$Pr$_{0.2}$Zr$_{0.1}$O$_{2-d}$ (CPZ). Both types can conduct both electrons and oxygen ions through the ceramic lattice. Most materials are better at conducting either electrons or oxygen ions. Mixed membranes are simply membranes made of a mixture of two or more materials, in order to take advantage of the best traits of each, e.g. 0.8ZrO$_2$0.1TiO$_2$0.1Y$_2$O$_3$ (ZTY). New materials are being created constantly, and there are many reports available on the properties of various oxygen ion transport membrane materials, as a number of different groups and individuals around the world are conducting research into this area. Fluorite membranes typically have a lower oxygen flux than perovskite membranes, but can withstand a much higher operating temperature. Perovskite membranes can typically conduct electrons more easily than ions, so that the ionic conductivity is a limiting factor. Zirconia (ZrO$_2$), on the other hand, can conduct ions more readily than electrons, so that the electronic conductivity is the limiting factor.

There are a number of factors that affect the passing of oxygen through the membrane. Initially the oxygen must reach the membrane. It is possible that due to transport in the flow of gas on the feed side of the membrane the flux could be limited. After the oxygen reaches the membrane it is adsorbed onto the surface. Surface exchange effects can limit the oxygen flux. The oxygen takes electrons from the material and the O$_2$ molecules split into O$^-$ ions. The oxygen is then transported through the ceramic by bulk transport as governed by Equation 1. Surface exchange at the permeate side of the membrane and transport of oxygen from the surface can also
affect the flux. The ions and electrons can travel equally well in either direction through the bulk of the material, so if more ions enter the material on one side of the membrane (feed side) than the other (permeate side), there is a cumulative flow of oxygen from the feed side to the permeate side. This is why a high oxygen partial pressure difference affects the oxygen transport, as demonstrated by Equation 1. Use of an oxygen-consuming reaction at the permeate side drastically reduces the oxygen partial pressure on the permeate side of the membrane, by removing the oxygen almost as soon as it desorbs from the surface. Consequently use of such a reaction, e.g. combustion, increases the flux through the membrane. At high oxygen partial pressures the oxygen vacancies in the ceramic lattice are almost all filled. This can limit the oxygen flux.

2.4. Oxyfired Cycles Incorporating Oxygen Ion Transport Membranes

As previously mentioned, cryogenic air separation has a very detrimental effect on the efficiency of oxyfired cycles. Cryogenic air separation requires air to be compressed and then cooled to a very low temperature. The oxygen is then distilled and captured as a liquid. Because heat is removed from the compressed air, the expansion of the gas produces less energy than the compression requires. Power is also required to operate the heat exchangers which reduce the temperature, in addition to the power required for compression. However OTMs offer the possibility of oxygen production without such a large adverse effect on the efficiency. Because the air is heated for use in the OTM, the expansion of the air after separation can produce more power than the compression requires. The OTM can be effectively incorporated into the cycle in such a way that it aids in the conversion of heat to power. A well
developed example of an oxyfired plant incorporating OTMs is the AZEP (Advanced Zero Emission Power) cycle,\textsuperscript{35} shown in Figure 6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{azep_cycle.png}
\caption{The AZEP Oxyfired Cycle\textsuperscript{35}}
\end{figure}

MCM = Mixed Conducting Membrane (OTM), Q = Heat, HX = heat exchanger, BFW = Boiler Feed Water, HRSG = Heat Recovery Steam Generator

The exhaust from the combustion chamber is split: part is used to heat steam and air for power production, the remainder is mixed with oxygen in the OTM unit (MCM reactor) and returns to the combustion chamber as oxidant. This partial integration of combustion chamber and air separator allows the required heat for the OTM unit to be provided directly by combustion. The membrane wall simultaneously conducts oxygen to the fuel side and heat to the air side. The combustion does not occur adjacent to the membrane wall, so that the membrane does not have to withstand flames, but hot combustion products enter the OTM module at temperatures close to
the adiabatic combustion temperature. The main turbine is the oxygen-depleted air 
turbine (referred to in Figure 6 as the gas turbine). This turbine drives both the air 
compressor and the electrical generator. The combustion gases do not drive a turbine, 
and are used to provide heat to a bottoming Rankine cycle. After the boiler, the 
combustion products are cooled to condense out the water, leaving CO₂.

This cycle demonstrates the difficulty as well as the benefit of using OTMs to 
provide oxygen: the OTM cannot be heated to too high a temperature, but the 
combustion should occur at the highest possible temperature for high efficiency. The 
AZEP cycle was compared to a V94.3A combined cycle power plant, the efficiency of 
which is 57.9%. "The penalty in thermal efficiency for the AZEP... is 8.3 percentage 
points. This high loss is mainly due to the reduced turbine inlet temperature (1200°C) 
that causes significant power loss both in the gas turbine and in the steam cycle." 
The turbine inlet temperature can be increased by optional firing of additional fuel in 
the heated air stream before entry to the gas turbine. The combustion products of this 
additional firing are released to atmosphere. By adding enough extra fuel at this point 
the AZEP’s efficiency is claimed to increase from 49.6% to 53.4%, but in this case 
only 85% of the CO₂ is captured.36

An economic analysis of the AZEP cycle showed that a carbon emission tax of 
€31 – €40/ton would make the AZEP with 100% carbon capture as economically 
attractive as the V94.3A plant.37 This would also be the case if the cost of emitting a 
ton of carbon were €31 – €40 under an emissions trading scheme such as the European 
Union Emissions Trading Scheme. If an oxyfired plant cycle is to be economically 
competitive with existing cycles without incentives such as taxes or emissions credits 
it must have a similar efficiency. The worldwide capacity of gas fired power plants 
suitable for AZEP technology from 2020 was estimated to be in the range of 10s of
It was estimated in 2004 that the AZEP cycle could be commercially available in less than 10 years, given a market, however the AZEP group has since disbanded, although some of the individual members are continuing to research the technology.

The Oxycoal-AC cycle, developed in Aachen (AC) in Germany, also includes a membrane unit in which O is mixed with combustion products (CO₂ and H₂O). Pulverized coal is burned in this mixture to provide heat for a Rankine cycle. The combustion products are not expanded but provide heat to the air stream and a bottoming steam Rankine cycle. The bottoming cycle generates power, whereas the air turbine drives the compressor only. The system is shown in Figure 7. The efficiency for this cycle, 41%, was calculated based on a simulation using Ebsilon.

![Figure 7: The Oxycoal-AC Cycle](image)
Note the depleted air is described as N\textsubscript{2} in the diagram. In fact it is impossible for 100% of oxygen to be removed by the membrane; some must remain as the oxygen partial pressure on the feed side must be greater than that on the permeate side. Also, only O\textsubscript{2} has been removed from the air, so other elements remain, e.g. H\textsubscript{2}O, Argon (Ar), CO\textsubscript{2}.

Siemens Westinghouse and Praxair collaborated to develop an oxyfired fuel cell cycle.\textsuperscript{40} In a hydrocarbon-fuelled fuel cell, the fuel is fed to the anode side of a fuel cell and air to the cathode side. About 85% of the fuel is used in the fuel cell, and the gas leaving the anode side is normally mixed with the cathode gas (i.e. air) and they are burned together. The heat from combustion is used to preheat the incoming air and fuel, and also to partially reform the fuel. In the system described the anode gas is fed to one side of an OTM, with the cathode (air) gas on the other side. Oxygen passes through the membrane to completely oxidise the cathode gas stream, which then consists entirely of CO\textsubscript{2} and H\textsubscript{2}O. Fuel cell cycles are very efficient, so this cycle is a promising development in the area of oxyfired cycles.

2.5. The ZEITMOP cycle

The ZEITMOP\textsuperscript{14} cycle is an oxyfired power plant cycle concept developed by Evgeni Yantovski, a Ukrainian scientist and engineer. The ZEITMOP cycle is the main cycle investigated in this thesis. The original cycle consists of 3 turbines, one for
oxygen-depleted air, one for the combustion products, and a third for CO$_2$ recirculated through the system. The ZEITMOP cycle could be developed for all types of fossil fuels.

Figure 8: The ZEITMOP Cycle

Figure 8 shows clearly the flows and components in the original cycle. Methane (1) is compressed in compressor A (2) and burned in combustion chamber B in a mixture of O$_2$ and CO$_2$ (17). The exhaust products (3) are expanded in turbine C (4) and are then cooled in two heat exchangers D and E (5,6) before being further cooled in cooling tower F (7), causing the water in the combustion products to condense. The liquid water is separated in water separator G and removed (18) leaving almost pure CO$_2$ (8). The CO$_2$ is compressed in a three stage compressor H with intercooling in the cooling tower F to 210 bar (9-13) and the portion born of combustion is captured (19). The rest of the CO$_2$ (14) is heated in heat exchanger E (15) and expanded in turbine I (16) before entering the OTM unit J where it is mixed with O$_2$ (25), then returns to combustion chamber B (17). Air (20) is compressed in compressor K (21) and heated in heat exchanger D (22) before entering OTM unit J in which the O$_2$ required for combustion (25) is removed. As the OTM unit has no moving parts, no
work is done by or in it. Transfer of oxygen is caused by the difference in O\textsubscript{2} partial pressures across the membrane, which is caused by work-consuming processes elsewhere in the cycle. The hot oxygen-depleted air (23) is then expanded in turbine L before being discharged to atmosphere (24). This hot air is the only gas stream leaving the plant, and as nothing has been added to the air but heat, it is not an emission. The net effect on the gaseous atmosphere is the removal of some O\textsubscript{2} and the addition of some heat. The water and CO\textsubscript{2} from the combustion leave the plant as liquid; hence they are effluents, not emissions.

As it is impossible to remove 100\% of water in separator G, there will be some water (vapour and/or droplets) entering the compressor H. This water may react with the CO\textsubscript{2} to form carbonic acid. If natural gas, rather than pure methane, is the fuel, it is likely that some sulphur dioxide will also be present at entry to the compressor. Also, some gases resulting from imperfect combustion will be present, e.g. CO, excess O\textsubscript{2}. It will be neccessary to either remove some of these compounds or make changes to standard compressor design and the problem is not a trivial one. This thesis does not investigate this problem. These additional gases will finally leave the plant as impurities in the captured CO\textsubscript{2} and water streams, rather than as gaseous pollutants emitted to atmosphere. As the CO\textsubscript{2} is likely to be sequestered, the impurities in the CO\textsubscript{2} stream do not pose a problem for atmosphere, although any law which governs CO\textsubscript{2} sequestration may include purity requirements. The liquid water at 30\textdegreeC is not a pollutant although it may require some treatment, depending on the quantities of impurities in the stream. Again, this thesis does not investigate this requirement.

In the original ZEITMOP cycle (ZEITMOP-Separate) the OTM reactor is remote from the combustion chamber. After the separation of the combustion
products the CO₂ is cooled and compressed, then heated and expanded (i.e. a Rankine cycle) before entering the OTM to be mixed with O₂. This mixture then enters a separate combustion chamber. As a result, the ZEITMOP-Separate cycle can have a higher combustion temperature than the membrane can withstand. The upper limit of the turbine inlet temperature depends only on the turbine, not on the OTM reactor.

The use of CO₂ turbines is feasible. Work carried out on the Graz cycle by researchers at the Institute for Thermal Turbomachinery and Machine Dynamics at Graz University of Technology has significantly advanced the development of CO₂ turbines. During the development of the Graz cycle, the ratios of CO₂ and H₂O have altered a number of times. The highest fraction of CO₂ was 77% by mass. A very detailed analysis of a turbine expanding this mixture with inlet conditions of 1312°C and 40 bar is given by Jericha et al.

Dr. Roman Warchol performed a number of AspenPlus simulations of the ZEITMOP cycle using AspenPlus version 11.1 as part of the research for his PhD. Combustion temperatures between 1200°C and 1500°C were used, with the OTM unit operating at maximum temperatures of 750°C to 1000°C. The results of one such simulation were presented by Yantovski et al. The simulation was based on various assumptions, such as isentropic efficiencies of 85% - 89% for the various turbines and compressors, heat exchanger effectivenesses of 92% - 94%, and heat exchanger pinch points of 15°C – 28°C. The Equation of State of Span and Wagner, shown in Appendix A, was used to calculate the properties of CO₂. At a combustion temperature of 1400°C the maximum temperature in the OTM unit was 920°C, and the average temperature of the OTM unit, i.e. the mass-averaged temperature of the fluid
in the OTM, was 587°C. It was assumed that the OTM unit did not transfer heat from the air to the CO₂, other than the heat carried through the membrane by the O₂ passing through. It was also assumed that the OTM unit could withstand steep temperature gradients. A thermal efficiency of 50% was found for the ZEITMOP cycle using this simulation.¹⁴ Warchol also investigated the effect of adding a heat exchanger transferring heat from the air stream to the CO₂ stream. This was found to increase the efficiency of the cycle by 7% at a combustion temperature of 1200°C.¹⁵

A detailed simulation of the ZEITMOP cycle with and without the extra heat exchanger was presented at ECOS 2006⁴² based on AspenPlus simulations performed by Warchol¹⁵. The paper concluded that the optimal temperature of combustion was between 1400°C and 1430°C. The authors assumed an increase of 7% with the extra heat exchanger for all temperatures.

The OTM was modeled as a unit which removed some O₂ from the air, operating at temperatures between 750°C and 1000°C. The O₂ stream was then joined with a CO₂ stream.⁴² This means that the situation shown in Figure 9 (data for combustion temperature 1400°C) was modeled as shown in Figure 10.

Figure 9: OTM Unit Inlets and Outlets in ZEITMOP-Separate
This model therefore assumed that the temperature of the OTM material was 925°C, whereas the actual average temperature of the OTM material is closer to 780°C. One error introduced by this assumption was that the flux calculated by the model (assuming 925°C) would be higher than the actual flux (at 780°C). This error only affects the physical size of the OTM unit and not the efficiency of the cycle, so this does not affect the validity of the simulation as a whole.

A second error was introduced by the assumption in this simplified model that there is no heat transfer in the OTM unit itself. A third error was introduced by the treatment of the pressures. Extremely large pressure drops were calculated based on the removal of O₂ from the air and the mixing of low pressure O₂ and high pressure CO₂. The driving force in an OTM is the oxygen partial pressure; however the transfer of oxygen through the membrane occurs in the solid state. The total pressure of the gases on either side is not related to the fraction of oxygen passing through. The total pressures will be affected more by the physical design of the membrane unit itself.
Average values of $P_1$ and $P_2$ were calculated as 2.34 bar and 0.606 bar based on data published by Yantovski et al.\textsuperscript{42} for a combustion temperature of 1200°C. The value of $\ln(P_1/P_2)$ is therefore estimated as 1.35 for the ZEITMOP-Separate cycle.

## 2.6. Oxygen Ion Transport Membrane Reactors for Oxyfired Power Plants

The largest element of the AZEP cycle is the membrane reactor. The current design of the module incorporates combustion chambers (the red tubes in Figure 11) and OTM modules into the same chamber.

![Figure 11: Design for OTM Reactor for AZEP Cycle\textsuperscript{35}](image)
The reactor temperature is controlled by the temperature of combustion. The fragility of the materials under consideration mean that the temperature of the combustion must be relatively low (<1250°C), which limits the efficiency. In addition to this, the AZEP group have identified staged combustion using partial catalytic oxidation as the optimum method of achieving low temperature complete combustion.\textsuperscript{35} This complicated method of combustion brings its own engineering challenges. The OTM modules are based on an extruded ceramic monolith structure, shown in Figure 12. These modules, shown in Figure 13, have been manufactured and tested. The extruded ceramic is a porous support, which is then coated with a dense membrane, as shown in Figure 14.

![Figure 12: Extruded OTM Module Designed for AZEP Cycle\textsuperscript{35}](image)

MCM = Mixed Conducting Membrane (OTM), HEX = Heat Exchanger
Sundkvist et al.\textsuperscript{35} and Selimovic\textsuperscript{43} give comprehensive information on many aspects of the reactor development. Many of the engineering challenges for the reactor are similar to those faced by heat exchanger designers, for example improving the surface to volume ratio. Selimovic\textsuperscript{43} gives detailed information on the various options under consideration for the solution of these problems. He identifies counterflow as more effective than coflow, which is in accordance with heat exchanger theory, and also presents data on OTM materials. Table 2 shows comprehensive data on the reactor development.
The oxygen partial pressure at the inlet is 20.7 kPa, implying that the inlet air is at atmospheric pressure. Sundkvist and Eklund report that tests have shown that the system operates as expected to a pressure of 10 bar and a temperature of 900°C\(^\text{37}\).

In addition to the engineering challenges inherent in the design of the unit, the reactor also has high maintenance costs. It seems likely that the ceramic parts will have a life of 2.5 to 7.5 years\(^\text{37}\).

Renz et al. present detailed information on the design of the membrane reactor for the Oxycoal-AC cycle. Mechanical stability of the ceramic is again provided by using dense membranes on porous supports. Two shapes of OTMs are compared – tubular membranes with cross flow and planar membranes with counterflow, as shown in Figure 15. Tests have been conducted on prototype units, an example of which is shown in Figure 16. Detailed information on pressures and temperatures in the unit is presented by Renz et al., along with calculations of the stress in the ceramic\(^\text{38}\).
Siemens and Praxair have collaborated on a project aimed at developing an oxyfired Solid Oxide Fuel Cell (SOFC).\textsuperscript{40} On exit from the fuel cell the anode gas and cathode gas are kept separate and enter an OTM afterburner. Praxair were working on creating the OTM ceramic, and have since developed a number of materials like this
which are designed to oxidise (burn) fuel – creating the effect of burning the fuel in pure oxygen\textsuperscript{32}. To date no system like this has been built (to the author’s knowledge), although at least one patent for a similar system has been filed\textsuperscript{44}. The aim of the unit appeared to be ensuring completion of oxidation of anode gas, rather than use of the fully oxidised fuel stream to produce power. To the author’s knowledge, Praxair were developing OTM materials for this system with an operating temperature of 1000°C. The membrane combustion reactor for the Siemens/Praxair cycle was being developed by Praxair, who are focusing on a tubular membrane. The paper gives the results of many tests on the reactor. The collaborative effort has since ended and the project does not appear to be near commercialisation, although there may be ongoing unpublished research. Samples of similar tubes were purchased from Praxair for the experimental portion of this research.

All of the units described above could be used as a basis for a ZEITMOP-Separate OTM unit. However, none of these can withstand the high temperatures required for the ZEITMOP-Combined layout. The temperature of combustion in the AZEP module is only 1250°C, and the membrane is not in contact with the partial catalytic oxidation combustion process. Although the Praxair membrane is in contact with the combustion process, the operating temperature of the membrane is only 1000°C.

2.7. The ZEMPES cycle

Transport is one of the largest producers of CO\textsubscript{2} for most if not all countries, and Ireland is no exception. Private transport is the norm and the booming economy
has resulted in more cars than ever before on Ireland’s roads. Eliminating or even reducing carbon emissions from transport would bring the possibility of reaching the Kyoto target much closer.

Cryogenic oxygen production onboard a vehicle is likely to be unfeasible due to the vibration and other forces caused by motion, which are detrimental to distillation columns, so OTMs are the most attractive option for oxygen production onboard a vehicle. The Zero Emission Membrane Piston Engine System (ZEMPES) is an oxyfired internal combustion engine cycle, which uses the same oxyfiring technology as the ZEITMOP, burning hydrocarbon fuel in a piston engine, with a mixture of O₂, CO₂ and H₂O instead of air. After separation of the combustion products the CO₂ produced is compressed and stored onboard, while the liquid water may be stored onboard or injected into the depleted air stream and emitted to atmosphere. The O₂ required is produced by an OTM unit which produces a mixture of O₂ and exhaust gases (CO₂ and H₂O), which is returned to the piston engine as oxidant. The CO₂ produced by the combustion is not released to atmosphere but is captured and stored onboard for later sequestration. A compressor is required to provide compressed air for oxygen separation in the OTM reactor, and is powered by a turbine.

Many options for the ZEMPES cycle have been described. The addition of a supercharging turbine and an optional bottoming Rankine cycle increased the calculated thermodynamic efficiency from 28% to 44%, however the system became more complex. Other options for increasing the efficiency are increasing the proportion of fuel and oxygen in the engine (i.e. reducing the portion of CO₂) and using the waste heat to thermochemically recuperate the fuel before combustion. The highest calculated efficiency was 47%. Figure 17 shows the ZEMPES cycle with a
supercharging turbine, and the power balance and efficiency calculated for this option are shown in Table 3.

Figure 17: The ZEMPES Cycle

R = Radiator for cooling, OF = Oil Flow in piston engine and turbine shaft, PE = Piston Engine, DS = driveshaft, C3H8 = Propane fuel, CC = CO2 Compressor, WS = Water Separator, CL = one-way clutch, O2 = oxygen flow through membrane wall, HE = Heat Exchanger, ITMR = oxygen Ion Transport Membrane Reactor, T = Turbine, C = Compressor.
Propane fuel (C₃H₈) at point 6 is mixed with CO₂ and O₂ from point 16 and this mixture burns in the piston engine, producing power and a mixture of CO₂ and H₂O at point 8. This hot gas stream is expanded in turbine T1 and cooled in a heat exchanger to point 10. It is further cooled in a radiator and the water separator WS, in which the water is removed at point 20 leaving almost pure CO₂ at point 12. This CO₂ is then split, and a portion is compressed, cooled and stored onboard at point 19. The rest of the CO₂ at point 13 is compressed in compressor C2 and enters the OTM unit. O₂ from the air at point 3 travels through the membrane and mixes with the CO₂, producing the mixture at point 15 which acts as oxidant in the piston engine. Ambient air at point 1 is compressed and heated in a heat exchanger to point 3 before entering the OTM unit. Oxygen is separated from the air by the membranes, leaving a hot, high
pressure, nitrogen-rich stream of depleted air at point 4. This gas stream is expanded in a turbine before being exhausted at point 5.

The water removed from the system at point 20 may be stored onboard, or injected into the air stream, in which case it would be emitted as steam, making the only emission harmless H₂O (just as in a hydrogen vehicle). Alternatively it could be stored onboard for removal when the vehicle is refuelled, as is done with the CO₂, which must be stored onboard the vehicle. It is envisaged that the CO₂ would be stored onboard until the vehicle is refuelled. One possibility for storing CO₂ onboard is a dedicated tank. However, a different possibility for ZEMPES is the storage of liquid CO₂ in the fuel tank, so that only one heavy high-pressure vessel is required. The more fuel consumed, the more empty volume remains for CO₂. A small leak of either substance through a gap between the baffle and cylinder wall would not be dangerous due to the lack of reaction between the substances. The OTM will not provide oxygen when it is cold. One possibility for starting the engine is burning the fuel in air, and using the exhaust gases for heating the membrane, but not recirculating them to the engine. This would require allowing some emissions during startup.

2.8. Solid Oxide Fuel Cells

A fuel cell has an anode, a cathode and an electrolyte. The electrolyte in a Solid Oxide Fuel Cell (SOFC) is a solid oxide ceramic which has the ability to allow oxygen ions to transport through the ceramic at elevated temperatures (typically 700°C – 1000°C). In other words, it is an OTM with low electron transport capabilities, usually Yttria Stabilised Zirconia (YSZ). When there is an oxygen partial pressure gradient across the electrolyte (i.e. more oxygen on one side than the other), oxygen
will flow from one side of the electrolyte to the other. In this type of fuel cell the anode and cathode are porous. An oxygen containing gas (typically air) flows across the cathode and a fuel gas across the anode. Oxygen converts to oxygen ions at the cathode, taking electrons from the cathode, and converts back into oxygen gas at the anode, giving up electrons to the anode. The cathode and anode are connected by an external electrical circuit, through which electrons return from anode to cathode. In this way, the oxygen passing through the electrolyte forces electrons through the external circuit, creating electricity. The oxygen that passes through is consumed on the anode side by reaction with the fuel. The anode contains catalysts to control this reaction, so it is similar to combustion in that the products are oxidised or partially oxidised fuel, but it is not identical to combustion. Steam is also involved in this reaction, and when methane is the fuel, about 3 times as much steam by mole is present than methane. Some of the energy released by this reaction is converted to electrical power in the fuel cell. The rest of the energy is available as heat and raises the temperature of the anode (fuel) and cathode (air) gas streams. Currently available SOFCs have maximum temperatures of ~1000°C. Excess air is required to keep the cell below this temperature. Air/fuel ratios in some papers studied\textsuperscript{49, 50, 51} are between 3.5 and 5 times the stoichiometric amount of air.

The voltage in a SOFC is the Nernst Potential, which is caused by the imbalance in oxygen concentrations across the membrane. This is shown in Equation 2.
Equation 2: The Nernst Potential

There are various resistances in the cell which lead to a reduction in this voltage so that the actual voltage in the cell is lower than the Nernst Potential. For a methane fuelled cell, the actual voltage is typically about 0.61 V\textsuperscript{51}. Cells are connected in series to create higher voltages. The current is the charge carried by the electrons through the outer circuit, so is directly related to the molar flow rate of oxygen, as each oxygen molecule carries 4 electrons through the electrolyte, and hence forces 4 electrons around the outer circuit. Assuming a constant voltage, the power produced by the cell is therefore directly related to the molar flow rate of oxygen through the electrolyte, as electric power is simply voltage multiplied by current. In many analyses\textsuperscript{49, 50, 51} the voltage is assumed to be constant and this is assumed in the analysis presented here.

\[
V = \frac{RT}{4F} \ln \left( \frac{P_{O_2,c}}{P_{O_2,a}} \right)
\]

- \(F\): Faraday’s Constant
- \(P_{O_2,c}\): Oxygen Partial Pressure at the Cathode (Air Side)
- \(P_{O_2,a}\): Oxygen Partial Pressure at the Anode (Fuel Side), which depends on the equilibrium constants for the various reactions at the anode
- \(R\): Ideal Gas Constant
- \(T\): Absolute Temperature

Equation 2: The Nernst Potential\textsuperscript{52}
As the oxygen is continually used up in the reactions at the anode, the imbalance in oxygen levels (oxygen partial pressure gradient) remains high. If the concentration of fuel in the anode stream were low, the oxygen would no longer be quickly used up. This would reduce the power produced by the fuel cell. For this reason, some fuel must remain in the anode stream at exit from the cell. Typically 80-90% of the fuel is used in the cell.

In order to prevent coking (carbon formation which blocks the pores in the anode), some water must be present on the anode side. SOFC systems typically include recirculation of exhaust gases, external or internal reforming of methane, and heat exchangers.

### 2.9. Literature Review relating to OFFCET cycle

When the OFFCET cycle was first conceived by the author, a literature review and patent search were conducted to discover if such a cycle has previously been published or patented. None were found and a paper on the concept was published, including three variations of the concept, presented in Section 4.3 and initial calculations on the simplest option, presented as part of this research in Section 5.1.5. Since publication of this paper, publications describing a cycle using this concept were found, showing that the overall idea of the OFFCET is not novel, although the author invented it independently. However, although the simplest concept is not new, to the author’s knowledge at least one of the variations on the OFFCET, published as “OFFCET with steam turbine” and referred to in this thesis as OFFCSET, is a novel concept and has not before been published or patented.
2.10. Chemical Looping Combustion

Chemical looping combustion means combustion using an “oxygen carrier”, typically a metal. The metal is oxidized in a fluidised bed using air and the metal oxides are then reduced by fuel in a different fluidised bed. Although the original aim of chemical looping combustion was to increase combustion efficiency, this method of combustion is also a method of oxyfiring. Ishida and Jin have developed this concept for oxyfiring. A number of research groups are investigating chemical looping combustion and it is currently at the laboratory scale. Leithner presented a diagram, reprinted here as Figure 18, for a coal or biomass fired cycle using nickel as the oxygen carrier.

Figure 18: Coal or Biomass Oxyfired Chemical Looping Combustion Cycle with Metal as the Oxygen Carrier
Leithner demonstrated with a second diagram that this concept is similar to that of oxygen transport using oxygen ion transport ceramics. Leithner further demonstrates that this membrane could be a SOFC, which is clearly shown in Figure 19. The use of ceramic membranes instead of metal oxides removes the need for two of the circulating fluidised bed reactors.

Figure 19: Coal or Biomass Oxyfired Cycle with an OTM/SOFC as the Oxygen Carrier

Use of membranes is currently at a more advanced stage than chemical looping combustion. Whether the possible increase in combustion efficiency using chemical looping sufficiently compensates for the greater mechanical complexity of the cycle remains to be seen.

The US Department of Energy has granted funding to BOC group, who are using flue gas recycling to burn coal in a mixture of oxygen and flue gas: “BOC plans to apply its CAR (Ceramic Autothermal Recovery) oxygen production process
that uses the mineral Perovskite to absorb oxygen and subsequently release it in a circulating fluidized bed.” It seems that BOC are using perovskite as the oxygen carrier in a chemical looping system, but it is not clear whether perovskite powder is being used in a recirculating fluidised bed, or if a perovskite OTM is being used as a combustor, in a manner similar to the ZEITMOP-Combined cycle.
3. **Comparison of Oxygen Transport Membrane Materials**

Much research has been published on OTMs by academic research groups around the world, both as oxygen producers and when used with an oxygen-consuming reaction on the permeate side of the membrane. However, these studies have been conducted at different temperatures and oxygen partial pressures, using membranes with different thicknesses and surface geometries. All of these factors affect the oxygen flux through the membrane. The available information on a number of OTM materials has been compiled and a detailed comparison of these materials forms part of the current research.

In testing the oxygen flux without an oxygen consuming reaction on the permeate side of the membrane, an oxygen-containing gas e.g. air, was used on the feed side, and another gas, e.g. helium, was used on the permeate side. The flux was then measured by analysing the oxygen concentration at the exit of the permeate side. There were two methods used of testing the oxygen flux with an oxygen consuming reaction on the permeate side. One experiment involved a tubular membrane with a mixture of CO and CO$_2$ on the permeate side and air on the feed side. The oxygen flux was calculated by measuring the differences in oxygen content at the inlet and outlet. Most of the results presented here for OTMs used with an oxygen consuming reaction are for syngas production. The permeate side of the membrane was coated or packed with a catalyst and methane flowed across this side, while air flowed across the feed side. The oxygen flux was then measured by analysis of the gases at the outlet of the syngas stream. Not all materials are suitable for syngas production, as many react with H$_2$, a component of syngas. If an OTM unit were to be used in OFFCET-Combined, one of the possible configurations of the OFFCET cycle, described in
Section 4.3.2., it would be in contact with H\textsubscript{2}. Small amounts of H\textsubscript{2} are also present during combustion, so materials that are unstable in a H\textsubscript{2}-containing environment may be unsuitable for use in ZEITMOP-Combined. The available information on the stability of the materials in a hydrogen-containing environment is therefore also presented here.

3.1. Normalising the Results

Where possible the oxygen fluxes have been normalised to reduce the effect of experimental parameters on the comparison. One set of experiments\textsuperscript{58} found that the oxygen flux increased with feed side flow rate up to a flow rate of 150 mL/min. Below this value less oxygen was reaching the membrane than could pass though, i.e. transport to the surface was a limiting factor. Therefore all values used in this thesis from those experimental results are taken at feed side flow rates of more than 150 mL/min.

Oxygen flux is measured in different units. Some results are given in mL/(cm\textsuperscript{2} min), others in µmol/(cm\textsuperscript{2} s). It was assumed by the author that mL/(cm\textsuperscript{2} min) was at Standard Temperature and Pressure (STP). The ideal gas law was used to convert these results to µmol/(cm\textsuperscript{2} s). Wang et al.\textsuperscript{58} presented results in both mL/(cm\textsuperscript{2} min), and µmol/(cm\textsuperscript{2} s). It was found that the values converted to µmol/(cm\textsuperscript{2} s) using the ideal gas/STP assumption agreed with the reported µmol/(cm\textsuperscript{2} s) values to within ± 5\% accuracy, or to within +/- 0.1 µmol/(cm\textsuperscript{2} s), confirming that the ideal gas/STP assumption was reasonably correct.

Graphs of normalised flux as a function of temperature were generated for the materials compared. In theory the relationship between the flux and temperature is
linear, and in the literature this is shown to be reasonably true in practice. Therefore linear interpolation, or simply reading the desired value off a line drawn on a graph, was used when required.

This comparison normalises the results to 1 mm membrane thickness, except where thickness is stated. In cases where information was available for samples of thicknesses greater and lesser than 1 mm, interpolation was used to estimate the flux at a physical thickness of 1 mm. In other cases, the flux was multiplied by the thickness in mm. Flux is inversely proportional to the thickness of the membrane, so this should normalise to 1 mm thickness.

Surface exchange effects can be identified by a difference in the normalised values for different thicknesses of the same material. Diethelm et al.\textsuperscript{59} normalised the flux through Ca\textsubscript{0.6}La\textsubscript{0.4}Fe\textsubscript{0.75}Co\textsubscript{0.25}O\textsubscript{3-d} (CLFC) membranes of different thicknesses to a thickness of 1 mm. As the results were at the same temperature and similar partial pressure differences, almost identical results were expected, yet higher normalised results were found for a membrane 1.745 mm thick than one 0.716 mm thick. This implies that surface exchange effects were slowing down the oxygen transport, i.e. oxygen could travel through the bulk of the material faster than it could be adsorbed onto the surface. This limit did not reduce the flux through the thicker material to the same extent as the thinner, as there was less travelling through the thicker sample in any case. This was obvious as the normalised flux through the thinner membrane is lower than the normalised flux through the thicker. One method for combating surface exchange limitations is to increase the surface area by adding an “activation layer”, a thin porous layer of the same material. It was found that bulk transport was the
limiting factor for SrCo$_{0.9}$Nb$_{0.1}$O$_{3-d}$ (SCN) membranes only about 50μm thick when a 5μm thick activation layer was used.$^{31}$

### 3.2. Comparison of Perovskite OTMs

The perovskite materials compared and the relevant references are shown in Table 4. Unfortunately industrial companies do not publish detailed results of their own research, instead giving information such as the relative increase in oxygen flux during development, so it was not possible to include any industrial materials.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Author</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBCF</td>
<td>BaBi$<em>{0.4}$Co$</em>{0.2}$Fe$<em>{0.4}$O$</em>{3-d}$</td>
<td>Shao et al.</td>
<td>2000</td>
<td>60</td>
</tr>
<tr>
<td>BCF</td>
<td>BaCe$<em>{0.15}$Fe$</em>{0.85}$O$_{3-d}$</td>
<td>Zhu et al.</td>
<td>2004</td>
<td>61</td>
</tr>
<tr>
<td>BSCF</td>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-d}$</td>
<td>Wang et al.</td>
<td>2002</td>
<td>30, 58</td>
</tr>
<tr>
<td>BTCF</td>
<td>BaTi$<em>{0.2}$Co$</em>{0.5}$Fe$<em>{0.3}$O$</em>{3-d}$</td>
<td>Tong et al.</td>
<td>2003</td>
<td>62</td>
</tr>
<tr>
<td>CLFC</td>
<td>Ca$<em>{0.6}$La$</em>{0.4}$Fe$<em>{0.75}$Co$</em>{0.25}$O$_{3-d}$</td>
<td>Diethelm et al.</td>
<td>2003</td>
<td>59</td>
</tr>
<tr>
<td>LCF</td>
<td>La$<em>{0.4}$Ca$</em>{0.6}$FeO$_{3-d}$</td>
<td>Diethelm et al.</td>
<td>2003</td>
<td>59</td>
</tr>
<tr>
<td>LCFC</td>
<td>La$<em>{0.6}$Ca$</em>{0.4}$Fe$<em>{0.75}$Co$</em>{0.25}$O$_{3-d}$</td>
<td>Diethelm et al.</td>
<td>2004</td>
<td>63</td>
</tr>
<tr>
<td>LSC</td>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.3}$O$</em>{3-d}$</td>
<td>Van der Haar</td>
<td>2001</td>
<td>34</td>
</tr>
<tr>
<td>LSCF</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_{3-d}$</td>
<td>Zhu et al.</td>
<td>2004</td>
<td>61</td>
</tr>
<tr>
<td>LSCF fibre</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_{3-d}$</td>
<td>Thursfield et al.</td>
<td>2006</td>
<td>64</td>
</tr>
<tr>
<td>LSGF</td>
<td>La$<em>{0.15}$Sr$</em>{0.85}$Ga$<em>{0.3}$Fe$</em>{0.7}$O$_{3-d}$</td>
<td>Zhu et al.</td>
<td>2004</td>
<td>61</td>
</tr>
<tr>
<td>LSGF-BSCF</td>
<td>12.8La$<em>{0.15}$Sr$</em>{0.85}$Ga$<em>{0.3}$Fe$</em>{0.7}$O$<em>{3-d}$ Ba$</em>{0.5}$Sr$<em>{0.5}$Fe$</em>{0.2}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-d}$</td>
<td>Wang et al.</td>
<td>2003</td>
<td>65</td>
</tr>
<tr>
<td>SCN</td>
<td>SrCo$<em>{0.9}$Nb$</em>{0.1}$O$_{3-d}$</td>
<td>Ito et al.</td>
<td>2007</td>
<td>29</td>
</tr>
<tr>
<td>SCT</td>
<td>SrCo$<em>{0.85}$Ti$</em>{0.15}$O$_{3-d}$</td>
<td>Kharton et al.</td>
<td>1999</td>
<td>66</td>
</tr>
<tr>
<td>SLFC</td>
<td>Sr$<em>{0.9}$La$</em>{0.1}$Fe$<em>{0.8}$Cr$</em>{0.2}$O$_{3-d}$</td>
<td>Kaus et al.</td>
<td>2007</td>
<td>67</td>
</tr>
<tr>
<td>SLFCC</td>
<td>Sr$<em>{0.8}$La$</em>{0.2}$Fe$<em>{0.7}$Cr$</em>{0.2}$Co$<em>{0.1}$O$</em>{3-d}$</td>
<td>Stephens et al.</td>
<td>2000</td>
<td>31</td>
</tr>
<tr>
<td>SLFT</td>
<td>Sr$<em>{0.8}$La$</em>{0.2}$Fe$<em>{0.8}$Ti$</em>{0.2}$O$_{3-d}$</td>
<td>Kaus et al.</td>
<td>2007</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 4: Perovskite Materials Compared
According to Equation 1, the flux is theoretically proportional to \( \ln(P_1/P_2) \), where \( P_1 \) and \( P_2 \) are the partial pressures of oxygen on the feed side and the permeate side respectively. However, in experiments it is easy to maintain \( P_1 \) constant, but very hard to ensure \( P_2 \) is constant along the membrane. Values for \( P_1 \) were available for all the materials, but values for \( P_2 \) were not, so most results could not be normalised to a particular partial pressure ratio. However, there is a relationship between \( P_1 \) and flux, albeit not a linear one. In the absence of information on \( P_2 \), it was decided to normalise the results to \( P_1 = 0.213 \) bar instead of normalising to a particular partial pressure ratio. This value was chosen as it is the atmospheric oxygen partial pressure. Most experiments provided results for this partial pressure. Some references did provide information on \( P_2 \), and these are discussed in section 3.2.2.

### 3.2.1. Comparison of Previously Published Oxygen Fluxes for some Perovskite Membranes in Oxygen Production Mode

Figure 20 shows fluxes for a number of materials when air is present on the feed side, and an inert gas is present on the permeate side. This is referred to as oxygen permeation mode.

It appears BSCF has the highest flux in oxygen permeation mode, and therefore an OTM unit composed of BSCF would be the smallest physical unit for production of a mixture of oxygen and an inert gas, all other parameters being equal. Geometries used in experiments were discs unless otherwise stated. Most materials’ fluxes have a discernible linear relationship with Temperature.
3.2.2. Variation of Oxygen Flux with Oxygen Partial Pressure Ratio

Figure 20: Oxygen Flux Compared to Temperature for some Perovskite Materials

References as in Table 4

Figure 21: Oxygen Flux Compared to Variation in Oxygen Partial Pressure Difference for some Perovskite Materials

References as in Table 4
Figure 21 shows the oxygen flux for those perovskite materials for which the value of $P_2$ is known. In the experiments performed on SCN\textsuperscript{29} pure oxygen at high pressure was used on the feed side of the membrane, with pure oxygen at atmospheric pressure (1.01325 bar) on the permeate side. The other materials shown in Figure 21 were tested with air on the feed side and an inert gas on the permeate side. The value for $P_2$ was assumed to be the partial pressure of oxygen at the outlet of the rig. This assumption was found to be valid in one set of experiments\textsuperscript{66}. Some materials were tested with different flow rates at the same temperature, providing a number of values for these temperatures. The materials without a stated temperature were tested with the same feed side flow rate at various temperatures and values are shown here for 700°C, 875°C and 915°C. The flux appears to fall with increasing partial pressure ratio for these materials, however this is because the highest oxygen flux was at the highest temperature, so that the highest value of $P_2$ and hence the lowest value of $P_1/P_2$ was at the highest temperature. If more extensive testing were performed, it is likely that a series of positive linear relationships would appear, intersecting the negative linear relationship shown on the graph at the data points shown.

The log of the partial pressure ratio was very low for the SCN tests. The dotted red and blue lines in Figures 21 and 22 represent the projected flux for SCN at higher partial pressure ratios. The oxygen flux of a 1 mm thick SCN membrane at a temperature of 875°C and a value of $\ln(P_1/P_2)$ of 1.35 is estimated to be 0.8 $\mu$mol/(cm$^2$s).

The dotted green and purple lines in Figure 21 represent the projected flux for the BSCF membrane. The line of closest fit intersects the origin at a higher value than 1.35, which implies that the flux would be zero at 1.35. This is an unrealistic estimate,
so a second method of linear projection was used, including the origin as a data point. This provides an estimate for BSCF of 0.5 \( \mu \text{mol}/(\text{cm}^2\text{s}) \) at 900°C and a value of \( \ln(P_1/P_2) \) of 1.35. A flux of 0.8 \( \mu \text{mol}/(\text{cm}^2\text{s}) \) is therefore estimated for a 1 mm thick OTM unit for the ZEITMOP-Separate cycle operating at a temperature of 875°C.

When an oxygen-consuming reaction is present on the permeate side, \( P_2 \) is very low, so the partial pressure ratio is extremely high. The value of \( P_2 \) with an oxygen consuming reaction was known for only two materials. Figure 22 shows the flux compared to variation in partial pressure ratio with and without an oxygen-consuming reaction on the permeate side of the membrane. The effect of an oxygen consuming reaction is discussed in more detail in Section 3.2.4.

Figure 22: Oxygen Flux Compared to Variation in Oxygen Partial Pressure Difference With and Without an Oxygen Consuming Reaction on the Permeate Side of the Membrane

References as in Table 4
3.2.3. Stability in a Hydrogen-Containing Atmosphere

The following materials have been tested in an environment containing hydrogen:

- **BSCF**: Structure destroyed, recovered by oxidation.
- **BTCF**: Structure destroyed, recovered after ½ hour in 1% Oxygen.
- **BCF**: Maintains structure at 900°C in hydrogen containing environment.
- **CLFC**: Flux measured in hydrogen environment, degraded from 0.8 μmol/cm²s to 0.6 μmol/cm²s. Remained constant at 0.6, even after thermal cycle.
- **LCF**: After 600 hours, surface exposed to H₂ decomposed but bulk unchanged and flux stable.
- **LCFC**: Stable in syngas production for 10 days, although some demixing occurred.
- **LSCF fibre**: When used to oxidise methane, some hydrogen was produced. There were periodic fluctuations in flux and some carbon (and probably some hydrogen) was deposited in or on the membrane. After use in methane mode, the material was again tested in oxygen permeation mode. The permeation flux was only half of the original flux, but then increased slowly to the original value, implying that the carbon and hydrogen deposits were being oxidised. A large amount of oxygen was also consumed by the membrane, which reduced over time. This implies that oxygen had been lost from the membrane when used in methane mode, i.e. that the material had degraded, but was replenished with oxygen over 95 hours. After 95 hours a sharp increase in the oxygen consumed was observed. This implies that there had been a change in phase of the material. It is also possible that some or all of the
irregularities were caused by contaminants. The authors note that previous tests on LSCF showed that it took about 20 hours for steady state fluxes to be reached, implying that it takes some time for steady state oxygen vacancy distribution to be reached.

<table>
<thead>
<tr>
<th>LSGF</th>
<th>Used to produce syngas for more than a year with no degradation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGF-BSCF</td>
<td>Maintains structure at 900°C in hydrogen containing environment.</td>
</tr>
<tr>
<td>SLFC</td>
<td>Production of secondary phases on surfaces but no degradation of flux.</td>
</tr>
<tr>
<td>SCF</td>
<td>Structure destroyed, 99.4% recovered after 16 hours in 1% Oxygen.</td>
</tr>
<tr>
<td>SLFT</td>
<td>Production of secondary phases on surfaces but no degradation of flux.</td>
</tr>
</tbody>
</table>

### 3.2.4. Flux With an Oxygen Consuming Reaction Occurring on the Permeate Side of the Membrane

Values were provided for oxygen flux in syngas producing mode for two of the materials, BSCF and LCFC. A third material, SLFCC, was tested with a mixture of CO₂ and CO on the permeate side. The highest percentage of CO was 89.7%, for which the value of flux is shown in Figure 23. A fourth material, LSCF, was manufactured as a hollow fibre, with an outer diameter of 1 mm and a thickness of 250 μm. This material was used to oxidise a mixture of 2.2% methane in helium. Two other materials, SLFT and SLFC, were tested with fuel mixtures containing H₂, CO and CO₂. These materials are compared in Figure 23.
Flux with an oxygen consuming reaction at the permeate side, 
\( P1 = 0.213 \text{ bar}, L = 1 \text{ mm} \)

\[\text{flux [\mu mol/cm}^2\text{s]}\]

Figure 23: Oxygen Flux Compared to Temperature With an Oxygen-Consuming 
Reaction on the Permeate Side of the Membrane for some Perovskite Materials

References as in Table 4

Again BSCF is the material with the highest flux. This is surprising, as BSCF 
is unstable in a hydrogen-containing environment and it was not only successfully 
used to produce syngas, but remained stable for 500 hours. The catalyst was then 
examined and it was discovered that the reaction had followed the combustion and 
reforming mechanism of syngas formation, described in Equation 3. The methane 
reacted with the oxygen at the membrane surface, forming CO\(_2\) and H\(_2\)O, which then 
reacted with the methane in the centre of the tube. No hydrogen reached the 
membrane surface, so the membrane was not actually in a reducing environment. 
There is another mechanism by which syngas may be formed, the direct partial 
oxidation mechanism, described in Equation 4. This would allow hydrogen in contact 
with the membrane surface.
Wang et al.\textsuperscript{30} state that at low space velocity ($<10^5$ L/kg h), the reaction would follow the combustion and reforming mechanism, while above this value, it would follow the direct partial oxidation mechanism. So a membrane that is unstable in a hydrogen environment can successfully be used as a syngas reactor if the space velocity is below this value. Above this value a membrane that is stable in a reducing environment is required for syngas production.

When an exothermic reaction occurs, there will be different temperatures at different points in the membrane. This will cause the flux to vary along the membrane. Stephens et al.\textsuperscript{31} found that the average flux through a membrane with varying temperature (average $= T_a$) was equal to the flux through the membrane when the temperature was $T_a$ along the membrane, when the outlet partial pressure ratio was equal. This implies that assuming an average flux for a tubular unit based on an average temperature is an acceptable assumption.
3.2.5. Comparison of Fluxes With and Without Reaction

Figure 24 shows the values of flux for BSCF and LCFC in both syngas and oxygen producing modes. Values of flux for SLFCC are shown for a permeate side gas containing 89.7% CO with the remainder CO₂ (SLFCC CO) and for a permeate gas containing 92% CO₂ with the remainder CO (SLFCC CO₂). The reaction on the permeate side of the LSCF hollow fibre membrane (LSCF fibre CH₄) was methane conversion i.e. combustion. Only 2.2% methane in helium was used in this experiment. The flux for the LSCF fibre is also shown in oxygen producing mode.

![Flux in both modes, P1 = 0.213 bar, L = 1 mm](image)

Figure 24: Oxygen Flux Compared to Temperature With and Without an Oxygen-Consuming Reaction on the Permeate Side of the Membrane for some Perovskite Materials

References as in Table 4
It is obvious that the flux is greatly increased by an oxygen-consuming reaction on the permeate side of the membrane. The actual increase is shown in ratio form in Figure 25.

![Graph showing ratio of flux in reaction mode to non-reaction mode](image)

Figure 25: Ratio of Oxygen Flux With and Without an Oxygen-Consuming Reaction on the Permeate Side of the Membrane for some Perovskite Materials

References as in Table 4

Although an 8-fold increase in flux was found during one particular test on BSCF, this graph, which compares representative normalised values, shows that a 6-fold increase when used with an oxygen-consuming reaction is a more realistic estimate. The LCFC material shows an even higher increase when used with an oxygen consuming reaction. The value for SLFCC is not the flux ratio for reaction: non reaction mode, but instead compares the flux for a high reaction rate to a low reaction rate. The value is included here for comparison only. The increase in flux for
LSCF fibre is quite low, most likely because only 2.2% methane was presented to the permeate side. However, even this small amount of methane almost doubles the flux.

### 3.2.6. Thickness

Most of the results seem to point to BSCF as the membrane material of choice. However, it is not yet commercially available. LSGF-BSCF has only been created in a disc 1.99 mm thick. LCFC, however, is commercially available in a tube only 0.2 mm thick. Figure 26 proves that BSCF really does have an exceptionally high flux. Even the 2 mm thick BSCF membrane surpasses the 0.25 mm thick LCFC membrane. The values of oxygen flux in Figure 26 have not been normalised, and are the actual values for the materials when $P_1 = 0.213$ bar.

![Flux in oxygen producing mode, $P_1 = 0.213$ bar](image)

**Figure 26:** Oxygen Flux Compared to Temperature Through Membranes with Different Physical Thicknesses for some Perovskite Materials

References as in Table 4
A thinner membrane has a higher flux, but it is physically weaker. Van der Haar\textsuperscript{34} created supported thin-film membranes – a dense membrane supported on a porous substrate of the same material. Using pulsed laser deposition, membranes as thin as 7.5 μm thick were created. These membranes can be created for any material. Mechanical tests showed that the substrate-supported thin film membranes could withstand absolute pressure differences of up to 30 bar\textsuperscript{34}. Ito et al. also produced thin-film membranes of a new material, SCN, with a thickness of about 50 μm. These were manufactured by dipping a porous tube in a slurry and firing at 1250°C, which produced a thin dense film on the porous substrate. A second porous layer, only about 5 μm thick, was then added on top of the dense layer. This was produced by coating with the slurry and sintering at 1100°C. The purpose of this “activation layer” is to increase O\textsubscript{2} surface exchange. The porous substrate also increases surface exchange on the inner side of the dense membrane. The results of the experiments show that the flux is dependant on transport of oxygen through the bulk of the material as governed by Equation 1, so the activation layers have performed well. These membranes withstood total pressure differences of 19.25 bar.

The fluxes in Figure 27 are the actual non-normalised fluxes. The value of $P_1$ is 0.213 bar for all the materials except for SCN, where $\ln(P_1/P_2) = 0.741$ and $P_2$ is 1.01325 bar. The natural log of the oxygen partial pressure ratio is lower for SCN than for any other material for which the value is known. This implies that normalising would only increase the gap between SCN and the other materials.
The supported thin-film membranes have much higher fluxes than the other membranes. The material LSC has an unremarkable level of flux when the thickness is of the order of 1 mm, yet supported thin-film membranes made of this material can surpass even the BSCF membrane. The flux for the 20 µm thick LSC membrane is actually higher than the flux for the 7.5 µm thick membrane, which implies that at the micrometer level, the bulk transport through the membrane as governed by Equation 1 is no longer the limiting factor for the flux for an LSC membrane without an activation layer.

The minimum thickness at which bulk transport is the limiting factor for oxygen flux (the critical thickness) can be estimated based on the chemistry of an individual material. It seems likely that the transport of oxygen through the bulk of the membrane would not be the limiting step for most thin-film membranes. Therefore
it is unlikely that the ratio of flux through LSC as a thin film versus a millimetre thick membrane can be used to predict the flux through any other material. No results are available for dense millimetre-thick SCN membranes, so no ratio is available for this material. Therefore no estimate can be made for flux through a thin-film BSCF membrane.

The normalised flux for the 47.3 μm thick SCN membrane is ~10 μmol/(cm² s) at 875°C and ln(P₁/P₂) = 0.741. An estimate of 18 μmol/(cm² s) can be made for a thin-film SCN membrane operating at 875°C and ln(P₁/P₂) = 1.35.

3.2.7. Maximum Operating Temperature

Perovskite ceramics are sintered as part of the manufacturing process. This involves maintaining the ceramic at a high temperature for a period of time in order to allow grain growth in the material. If the material is subsequently heated at or above this temperature, or even close to it, the material will begin to sinter again. This sintering may irreversibly alter the properties of the material. It will reduce the porosity of the porous substrates of thin-film membranes. At temperatures a few hundred degrees above the sintering temperature, the material will melt. The effect of this is that perovskites have maximum operating temperatures that are less than their sintering temperatures. The sintering temperatures are typically about 1200°C. Because of this perovskites are not suitable for use as OTMs at temperatures above 1000°C. The sintering temperature is typically a hundred or two hundred degrees below the melting temperature. For example, BSCF melts at 1180°C.
3.3. Comparison of Fluorite Membranes

Zirconia, ZrO$_2$, is a fluorite ion transport membrane, but is only in the fluorite phase above 2370°C. When it is stabilised with 8 – 9 mol % Yttria, Y$_2$O$_3$, it remains in fluorite form from room temperature to the melting point, which is higher than 2500°C$^{68}$. This Yttria Stabilised Zirconia (YSZ) has many applications in high-temperature industries, and is used as a coating for combustion chambers. It has high conductivity for oxygen ions at high temperatures, but lower electron conductivity. As electrons must travel back to the high oxygen side of the membrane to create more oxygen ions, this means the electron conductivity is a limiting factor for YSZ as an OTM. YSZ is the electrolyte of choice in SOFCs, because of its relatively high oxygen ion conductivity and low electron conductivity. While YSZ is perhaps the best known fluorite membrane, it is not suitable for use as an OTM because of its low electronic conductivity.

Fluorite membranes in general can withstand much higher temperatures than perovskite membranes; however their fluxes are lower. Much less information is available on fluorite membranes used as OTMs than on perovskite membranes. Figure 28 shows the fluxes of two fluorite materials designed for use as OTMs. The materials are listed in Table 5.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Author</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>Ce$<em>{0.7}$Pr$</em>{0.3}$O$_{2-d}$</td>
<td>Fagg et al.</td>
<td>2005</td>
<td>69</td>
</tr>
<tr>
<td>CPZ</td>
<td>Ce$<em>{0.7}$Pr$</em>{0.2}$Zr$<em>{0.1}$O$</em>{2-d}$</td>
<td>Fagg et al.</td>
<td>2005</td>
<td>69</td>
</tr>
<tr>
<td>ZTY</td>
<td>0.8ZrO$_2$0.1TiO$_2$0.1Y$_2$O$_3$</td>
<td>Arashi and Naito</td>
<td>1992</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 5: Fluorite Membranes Compared
The fluorite materials have low fluxes compared to perovskites. The dotted lines shown on the graph for CP and CPZ describe the expected flux at higher temperatures, assuming the flux rises linearly with temperature. The CP and CPZ materials were measured in oxygen permeation mode, and the ZTY material with an oxygen consuming reaction on the permeate side. It can be seen that the flux of ZTY, normalised to 1 mm thickness at 1400°C is about 0.17 μmol/(cm²s) when used with an oxygen-consuming reaction on the permeate side. It can be seen that the flux for CP at 1400°C is expected to be in the area of 0.12 μmol/(cm²s) when used in oxygen permeation mode. Assuming that this flux will increase 6-fold when used with an oxygen-consuming reaction, a flux of 0.72 μmol/(cm²s) at 1400°C for a 1 mm thick membrane seems to be an acceptable estimate for the best fluorite membranes currently in existence. Similarly, at 1300°C, a flux of 0.6 μmol/(cm²s) is estimated. Therefore a flux of 0.72 μmol/(cm²s) is estimated for a ZEITMOP-Combined unit.
operating at a combustion temperature of 1400°C. If the membrane was to be manufactured as a thin-film membrane, this flux would increase, however, as previously explained, it is impossible to say by how much.

Research on developing perovskites for use as OTMs has been ongoing for a number of years. There has been very little research so far into developing fluorites as OTMs. It is very likely that the fluxes of fluorite membranes will increase in the near future. No literature on thin-film fluorite membranes was found.
4. Methodology

4.1. Simulations

The ZEITMOP-Combined cycle has never before been investigated. Initial calculations were performed by the author on the ZEITMOP-Separate and ZEITMOP-Combined cycles. These implied that the two cycles have similar efficiencies. AspenPlus simulations were then performed on the ZEITMOP-Combined cycle.

Dr. Roman Warchol visited Dublin Institute of Technology as a postdoctoral researcher and collaborated on the AspenPlus simulations. His model of the ZEITMOP-Separate cycle was used as the basis for the ZEITMOP-Combined model. The author identified the previously mentioned errors in the previous OTM model and the simplified OTM model described in Section 5.2.2. was developed in collaboration. Dr. Warchol ran the simulations and collated some of the data. The author collated some of the data and analysed the results of the first simulations. The author conceived of a new OTM model. Dr. Warchol provided information on the capabilities of AspenPlus and the new OTM model described in Section 5.2.3. was developed in collaboration. Dr. Warchol developed the different AspenPlus models for the heat transfer from the air to the CO$_2$ stream, and ran the second simulations. The author compared the results of the first and second sets of simulations. The author compared the results of the ZEITMOP-Combined simulations to previously published research on the ZEITMOP-Separate cycle and analysed the results of the second simulations.

The calculations and simulations are described in detail in Chapter 5. The results are shown in Chapter 7.
4.2. Experimental Work

It was initially thought that experimental work would be a major part of the project. It was thought that experiments were required to:

a) confirm that combustion adjacent to an OTM is possible.

b) find out whether combined or separate combustion is preferable for the ZEITMOP cycle.

A rig was designed to burn fuel in an OTM tube and analyse the exhaust to measure the oxygen flux through the OTM material in both combustion and non-combustion modes. Samples of two types of OTM materials were purchased, and the rig was built. Experimental results were not acquired due to a number of problems.

In May 2005 Praxair published research proving that combustion adjacent to an OTM was possible and has been achieved\textsuperscript{32}. The results of the simulations performed as part of the current research clearly demonstrate that the effects of a combined unit on the overall ZEITMOP cycle can be analysed with simulation rather than experimental work. Therefore the two initial aims of the experiments no longer applied.

It was then thought that the contribution of the experimental work would have been a comparison of fluxes for two materials in combustion and non-combustion mode. The detailed comparison of previously published OTM materials undertaken as part of the current research provided extensive information on the fluxes of various OTM materials in reaction and non-reaction mode, and in one case in combustion mode.

The simulations show that a combined unit is not worthwhile for the ZEITMOP cycle unless it can operate at temperatures above 1200°C. The perovskite
material purchased was LaSrFeCr (of unspecified proportions), a perovskite that was designed for combustion by Praxair, however it has a maximum temperature of 1000°C, so is unsuitable for use in a combined OTM combustion unit for the ZEITMOP cycle. The fluorite material purchased was YSZ, which has very low oxygen conductivity without an external mechanism for electron transfer, so is also unsuitable for use in the ZEITMOP cycle, although consideration of the implications of this led to the invention of the OFFCET cycle.

Although it was clear that the experimental results were not required before the rig was completed, it was decided to continue with the experimental work while time allowed. However, results were never acquired. The work completed is presented in Chapter 6 as it may be useful to future research.

4.3. Oxygen Fired Fuel Cell Energy Turbine (OFFCET) Power Plant Cycle Concept

Oxygen ions are double negative, so in order to maintain electronic neutrality across an OTM, two electrons per ion must travel through the membrane in the opposite direction to the ions. YSZ has a very high oxygen conductivity and a very low electron conductivity, however it can withstand very high operating temperatures, so it was initially considered suitable for OTM combustion.

An experimental rig was considered in which electrons would be facilitated in returning from the permeate side to the feed side of the YSZ membrane, in order to increase the oxygen flux. While investigating possible methods of manufacturing such a rig, it became apparent that the design required was identical to a SOFC. Consideration of the implications of this led to the concept of using fuel cells as OTMs in an oxyfired power plant. This in turn led to development of the Oxygen Fired Fuel
Cell Energy Turbine (OFFCET) concept, which is presented in this thesis. Such a plant would produce electricity from the fuel cell in addition to electricity produced by the turbines.

4.3.1. Concept of OFFCET

Methane enters the fuel (anode) side of a SOFC. Air enters the oxidant (cathode) side. Oxygen travels through the electrolyte, and oxidises the fuel, releasing energy, some of which is directly converted to electricity in the cell, and the rest of which increases the temperature of the air and fuel streams. Not all of the fuel is oxidised in the fuel cell, and oxidation (combustion) is completed in an oxyfiring combustion chamber. Just as with the ZEITMOP cycle, it is possible to use either a combined OTM combustion chamber or an OTM air separator which extracts oxygen from the air, along with a separate combustion chamber. These options are called OFFCET-Combined and OFFCET-Separate. The fuel stream after combustion contains only CO\(_2\) and H\(_2\)O. The air stream is separated from the fuel stream at all times; only oxygen is removed from the air and only heat is added to it. The hot air and fuel streams are expanded in turbines to produce power, then cooled in heat exchangers (which heat the gases before entry to the fuel cell subsystem). The hot air from which some oxygen has been removed is the only emission from the plant. After the turbine the fuel gases are further cooled, condensing out the water, and the almost pure CO\(_2\) is then compressed with intercooling to a very high pressure for sequestration.

SOFCs require a high proportion of steam on the anode side of the cell. For the OFFCET cycle it was assumed that the fuel cell is a “block” operating at steady state. Recirculation, reforming, control of temperatures in the cell, mixing of methane

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with steam (through recirculation of anode gases) etc. are all internal to the fuel cell “block”. However, a third option was also considered in which the steam continues through the rest of the system, and is condensed, compressed and expanded in a bottoming Rankine cycle before returning to the SOFC. This option is called OFFCSET – Oxygen Fired Fuel Cell Steam Energy Turbine.

4.3.2. OFFCET-combined

Figure 29: OFFCET-Combined

Figure 29 shows the OFFCET-combined concept. Hydrocarbon fuel, e.g. methane, enters the system at a high pressure (1). It is heated in a heat exchanger (2) and expanded to the fuel cell operating pressure. Current SOFCs operate at 3-10 bar. The fuel enters the anode side of a fuel cell, in which it reacts with oxygen (25) and is heated (4). The partially oxidised gas, containing unreacted fuel, CO₂, H₂O, CO and
H₂, then enters the OTM combustion chamber. Oxygen (26) completes the combustion of the fuel, and the fuel stream now contains mainly CO₂ and H₂O, along with any excess O₂, and any other gases resulting from impurities in the fuel (5). This hot gas is expanded in a turbine (6) and cooled in heat exchangers (7, 8) and a cooling tower (9). The water in the exhaust is removed by condensation (16) and the CO₂ containing any impurities (10) is compressed with intercooling to a high pressure for sequestration (11-15). Any impurities are therefore sequestered along with the CO₂. Air (17) is compressed to the SOFC operating pressure (18) and heated (19, 20) before entering the SOFC. In the fuel cell, some oxygen (25) is removed from the air and the temperature of the air increases (21). The air then enters the OTM combustion chamber, in which more oxygen (26) is removed and the temperature increases further (22). The hot, high pressure air is expanded in a turbine (23) and then cooled (24) before being exhausted to atmosphere. This hot air from which some oxygen has been removed is the only emission from the plant. DC electrical power is produced in the SOFC, and other power is produced or consumed by the various turbines and compressors in the system.

4.3.3. OFFCET-Separate

The OFFCET-Separate cycle, shown in Figure 30, is essentially the same as OFFCET-Combined, with the exception that the OTM is separate from the combustion chamber. Oxygen (26) is removed from the air in the OTM, as in the previous cycle, however the gas on the permeate side is not the flammable SOFC anode gas (4), but some recirculated exhaust gases (27), which have been cooled to a temperature appropriate to the OTM material (28). These gases do not react with the oxygen passing through the membrane. The OTM can therefore operate at a lower
temperature than the combustion (conversely, the combustion can occur at a higher temperature than the OTM operating temperature). The mixture of exhaust gas and oxygen (29) enters a separate combustion chamber where the final combustion takes place. After removal of the oxygen, the air (22) is heated (30) before expansion. Figure 30 ignores the requirement for a compressor at point 29. This compressor would need to overcome the pressure losses in both the OTM and the heat exchanger.

It is necessary to have a gas flow on the permeate side of the OTM to ensure the oxygen partial pressure is lower on the permeate side than the feed (air) side. The amount of recirculated gas will affect both the combustion temperature and the temperature of the air at entry to the air turbine.

Figure 30: OFFCET-Separate
**4.3.4. OFFCSET**

A third possible layout is the OFFCET with recirculated water powering a steam turbine. This configuration is called OFFCSET – Oxygen Fired Fuel Cell Steam Energy Turbine, and is shown in Figure 31.

![Figure 31: OFFCSET](image)

In this case the water required in the fuel cell to prevent coking is not only recirculated within the cell itself, but within the outer system. The extra water remains with the products of combustion until the water is condensed out. Some water (28) is then pumped to a high pressure (29), heated (30) and expanded in a steam turbine to the fuel cell operating pressure (31) before being mixed with the fuel and re-entering the fuel side of the system (19). The advantage of this is that the water used to prevent coking is also used to produce work.
4.3.5. Other Possibilities for the OFFCET cycle

The pressure on the air side of the fuel cell may be different from the pressure on the fuel side, depending on the fuel cell design. It would be possible to recirculate CO₂ and use it to produce work, as in the ZEITMOP system.

It has been assumed that the air stream exits the SOFC at a temperature 15°C less than the exit temperature of the fuel stream. However, exit temperatures from the SOFC may be significantly different for fuel and air sides, depending on whether the fuel cell operates in a coflow or counterflow arrangement.

A possible startup option is to store pure oxygen on the premises (either from an external source or by adding an oxygen producing unit) and inject this oxygen into the fuel side of the cell until the system has heated up. The oxygen can be either pure or mixed with CO₂ or H₂O or both as a dilutant.

Extra fuel may be injected into the combustion chamber. This would increase the turbine inlet temperature. As the fuel cell section of the system would likely have a higher efficiency than the turbine section, it is unlikely that this will be the optimal layout.

In the OFFCET-Separate cycle the OTM could be used to produce pure oxygen, eliminating the need for exhaust gas recirculation. If the OTM were to produce pure oxygen, the total pressure of the oxygen produced would be less than the partial pressure of the oxygen on the air side of the OTM. This would be possible if the total pressure at the air side of the OTM were more than 5 times the total pressure on the permeate side. The pure oxygen could then be compressed to the combustion chamber pressure, or alternatively the entire fuel stream could operate at a lower pressure than the air stream. Use of pure oxygen would produce the hottest possible exhaust gas stream. Depending on the turbine used, this may be a viable option.
Other types of OTMs can produce pure oxygen at pressures higher than the oxygen partial pressure on the feed side, by forcing electrons through an outer circuit from the permeate side to the feed side. This is essentially a fuel cell in reverse, using electricity to force oxygen through the membrane (a fuel cell uses the oxygen flow through the membrane to force electrons through the outer circuit).

The condensing pressure (and temperature) used in the OFFCSET cycle should be as low as possible. Modern steam plants use lower than atmospheric condensing pressures. The water born of combustion may be condensed, pumped and injected into the air stream to increase the work done by the air turbine. It is possible that this water could contain dissolved impurities, depending on the purity of the fuel. It could also contain dissolved CO₂.

4.4. Work done on ZEMPES cycle

4.4.1. Size of OTM unit

The OTM unit required for the ZEMPES configuration with a bottoming Rankine cycle must provide 1.85 mol/s oxygen from 15 mol/s air at 7.09 bar and 787°C, to 7 mol/s CO₂ at 2.59 bar and 110°C. The working temperature of the OTM was taken to be 787°C. The air enters with an oxygen partial pressure of 1.49 bar, and leaves with an oxygen partial pressure of 0.7 bar. The average feed side oxygen partial pressure (P₁) is therefore 1.1 bar. The CO₂ flow enters with an oxygen partial pressure of 0 bar and leaves with an oxygen partial pressure of 0.54 bar. The average permeate side oxygen partial pressure (P₂) is therefore 0.27 bar. This situation is demonstrated in Figure 32. Wang et al. presented results for the oxygen flux through a BSCF membrane as a function of \( \ln(P₁/P₂) \). Assuming a temperature of 787°C and a thickness of 0.17 mm, the flux is estimated as 6.05 \( \mu \)mol/(cm² s). For 1.85 mol/s, ~
300 000 cm² would be required. Assuming tubes 7 mm in diameter, the overall size of the OTM unit required was estimated as 53 cm x 53 cm x 50 cm. This is large, but acceptable for a commercial vehicle. Although some of the assumptions used are inaccurate, this estimation provides a general idea of the size of the unit.

![Diagram of OTM Unit for the ZEMPES cycle](image)

Figure 32: OTM Unit for the ZEMPES cycle

### 4.4.2. Design of Mechanical System

A mechanical design for the ZEMPES has never before been considered. This thesis presents the first mechanical design for the ZEMPES. This design was developed as a Final Year Project under the supervision of the author. The piston engine may be a spark or compression ignition engine. Of the various options for the ZEMPES, the configuration shown in Figure 17 was chosen for the mechanical design. The size of the OTM unit used in the mechanical design presented here is that calculated above. The system layout was designed using Solidworks. Many aspects of the system were considered, such as the size of components, placing of components to minimise undesirable heat losses and minimising the overall size.

The various turbines and compressors are assumed in the original thermodynamic design to operate on one shaft, which provides extra energy to the
driveshaft by means of a clutch. This is an unsatisfactory arrangement for a real world system, as the turbines and compressors would operate at significantly different speeds to the piston engine shaft, and would likely operate at different speeds to each other. However, there is a number of other possibilities for the layout of the system. One possibility is to link one turbine and one compressor on one shaft, with the other turbine and compressor on a second, and the piston engine on a third. The power from the three shafts could be combined using planetary gear systems, which allow two shafts operating at different speeds to provide power to another shaft operating at another speed. There would therefore be two planetary gearboxes in addition to the normal vehicle gearbox. Another possibility would be to use one of the turbines (T2) to power the two compressors and use only one turbine (T1) and the piston engine to power the driveshaft. All of these options would have to overcome the significant difficulties caused by adding power from two shafts operating at very different speeds. A different approach would be to use the turbines and compressors to generate electricity, driving a motor, which powers a shaft at a speed similar to the piston engine shaft. However, the option chosen for this initial design is to use the two turbines to power the two compressors and use only the piston engine to power the driveshaft. The reason for this decision was that the system was being designed with a prototype in mind, simplifying as far as possible. Turbine 1 and compressor 2 are joined in this manner and turbine 2 with compressor 1. One result of combining the turbines and compressors in this manner is that the energy produced by the turbines is not used to power the vehicle, only to power the compressors. This reduces the efficiency, but greatly simplifies the system, removing the need to combine power from two or three different shafts.
The design was modelled on the rear end of a bus chassis. Figures 33 and 34 show the design from the rear wheels to the rear of the bus chassis. As can be seen, it is a reasonable size for a bus.

R = Radiator, T = Turbine, C = Compressor, ITMR = OTM unit

Figure 33: Mechanical Design of ZEMPES

The piston engine shown in the drawings is a simplified drawing of a commercially available propane gas piston engine of an appropriate size. The turbocompressors are based on commercially available vehicle turbocompressors. The other parts in the system have been sized and positioned, but not designed in great detail. Using turbocompressors in this manner has allowed the mechanical design to be developed in as simple a manner as possible, however it results in a reduction in
efficiency of 11 percentage points, as shown in Table 6. This is a 30% reduction in the power of the engine.

Figure 34: Three Dimensional View of ZEMPES

| Power balance for fuel energy flow 756.28 kW |  |
| Indicated power | 270.11 |
| Friction losses | -14.29 |
| Gases exchange | -20.00 |
| Radiator fans power | -20.70 |
| CO₂ liquefaction compressor | -20.00 |
| Effective power of the ZEMPES | 195.12 |
| Efficiency = effective power/fuel energy | 25.80% |

Table 6: Power Balance and Efficiency of Mechanical Design for ZEMPES
4.4.3. Further Consideration of the ZEMPES Cycle

Use of a combined storage tank for CO$_2$ and propane eliminates the need for two heavy high-pressure storage tanks onboard the vehicle. A cylindrical tank could be equipped with a sliding baffle, which moves slowly inside the tank as fuel is gradually consumed, allowing CO$_2$ to occupy the volume. When the tank is filled with propane the pressure will be different to when the tank is filled with CO$_2$. As the propane is used up, CO$_2$ is pumped into the tank by the onboard CO$_2$ compressor. If a rotary compressor of sufficient power is used, the CO$_2$ will automatically enter the tank at a pressure just high enough to increase the CO$_2$ volume and decrease the propane volume. The pressure on both sides of the baffle will always be equal, and the pressure in the tank should change smoothly from the pressure for 100% propane to the pressure at 100% CO$_2$, whether this is an increase or a decrease. The carburettor or other gas delivery system that delivers the propane to the engine must be able to withstand this change in pressure. When the volume of propane is quickly reduced (during acceleration) the pressure in the tank may change quickly, which could affect the compressor. It is unlikely that this effect would be noticeable considering the small amount of propane that would be removed compared to the size of the tank.

At a filling station the stored onboard CO$_2$ can be discharged into a central tank to be sequestered while new fuel enters the same tank. This central tank could also be used for joint fuel and CO$_2$ storage, with similar tanks in the trucks used to deliver fuel, and so on. This means that the CO$_2$ could be delivered back to the initial source of the fuel without incurring any extra mileage. Such a situation, where CO$_2$ is returned when fuel is purchased, would integrate well with economic incentives for carbon sequestration, as the price of the CO$_2$ could be deducted from the price of the fuel, allowing users to see the benefit of carbon sequestration in their own pockets.
This situation would occur if CO$_2$ has a positive market value, which could happen in a number of situations e.g. in a carbon tax situation, a situation in which a significant amount of CO$_2$ is required by industry (including EOR and ECBM), or a situation in which companies have a carbon emissions quota, which can be increased by sequestering external CO$_2$.

For methane the mass of CO$_2$ produced by stoichiometric combustion is 2.75 times the mass of fuel, for ethane it is 2.93 times, and for propane it is 3 times the mass. This means that if all the CO$_2$ is stored onboard, the vehicle will get heavier rather than lighter as fuel is used up. This would also increase the cost of transportation for the delivery of fuel, as the fuel trucks would also become heavier as they deliver fuel.

If emissions are allowed during startup, measuring the CO$_2$ stored onboard would allow easy tracking of these emissions. Alternatively some oxidant (oxygen mixed with combustion gases) could be stored onboard for oxyfired combustion during startup, and replenished when the system reaches a high enough temperature. Control of this could be easily implemented using pressure sensors; however another high-pressure tank would be required.
5. Simulations

This thesis presents an investigation into the impact of combining the OTM air separator and the combustion chamber in the ZEITMOP cycle, i.e. burning fuel on the permeate side of the OTM membrane. This has been named the ZEITMOP-Combined cycle, which is shown in Figure 35.

Figure 35: ZEITMOP-Combined

This cycle has never before been investigated. Initial excel calculations were performed on various options for the ZEITMOP cycle. Initial excel calculations were also performed on the OFFCET-Combined cycle. AspenPlus simulations were performed on the ZEITMOP-Combined cycle using two different models for the OTM/combustion chamber unit. All efficiencies calculated for this work are based on the lower heating value of the fuel. The results are shown per kmol of methane, but this does not mean that an actual plant would be this size. There are no 366 MW SOFC plants, for example.
5.1. Initial Calculations

5.1.1. Initial Thermodynamic Calculations on the Efficiency of the ZEITMOP-Separate and ZEITMOP-Combined Cycles

As this is the first time the ZEITMOP-Combined cycle has been simulated, the author first performed simplified excel-based simulations of the ZEITMOP-Separate and ZEITMOP-Combined cycles for the purposes of comparison. Simplifying assumptions were used for these simplified thermodynamic calculations. These assumptions are in accordance with the first law of thermodynamics but as some of them ignore losses, they violate the second law of thermodynamics. As the same assumptions apply to ZEITMOP-Separate as to ZEITMOP-Combined, the results should be directly comparable to each other, but should not be compared to more rigorous analyses.

The simplifying assumptions are:

- isentropic turbines and compressors with no blade cooling ($PV^\gamma$ is constant)
- all the heat removed from one stream in a heat exchanger enters the other stream(s)
- 15ºC pinch points in heat exchangers
- no pressure losses in the combustion chamber, OTM unit or heat exchangers
- complete stoichiometric combustion without dissociation
- constant specific heat ratios
- the OTM unit does not transfer heat from the air to the CO₂
- the OTM unit can sustain steep temperature gradients
- 20% excess air enters the OTM unit
- the stoichiometric amount of oxygen is removed from the air by the OTM unit
Many of these assumptions increase the calculated efficiency. In order to compensate for this increase, two further assumptions were made:

- The turbine work was assumed to be 90% of isentropic.
- The compressor work was assumed to be 117% of isentropic.

In reality this “lost” work would remain as enthalpy in the fluid, so these final assumptions compensate for more than just the isentropic assumption.

The simplified calculations were performed as followed:

- Volumes were calculated using the ideal gas law, except for liquid water, the volume of which was assumed to be 0.001 m$^3$/kg at all temperatures.
- Temperature changes and work performed during isentropic processes were calculated using the assumption that $PV^\gamma$ is constant for an isentropic process, the ideal gas law and the definition of work. These combine to form the standard formula for isentropic work shown in Equation 5.

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$W$ = isentropic work

$P_1$ = Pressure at start of process

$V_1$ = Volume at start of process

$P_2$ = Pressure at end of process

$V_2$ = Volume at end of process

$\gamma$ = Ratio of specific heats for material

Equation 5: Isentropic Work
• In the heat exchangers, the total enthalpy change in one fluid stream was calculated by multiplying the specific heat capacity of the material, the mass and the change in temperature. Values for specific heat capacity were assumed to be the average across the temperature range. The specific heat capacity for a mixture of fluids was assumed to be the mass-averaged specific heat capacity. The total enthalpy removed from one stream was added to the other stream(s).

• The combustion temperature was assumed to be the adiabatic combustion temperature, which was calculated using the assumption that total enthalpy into the combustion chamber is equal to total enthalpy out. The enthalpy values were calculated using standard combustion tables. The quantity of recirculated carbon dioxide required to achieve the required combustion temperature was calculated iteratively.

• In the OTM unit of the ZEITMOP-Separate cycle and the ZEITMOP-Combined cycle, the temperature of the oxygen-depleted air exiting the OTM unit was kept identical to the temperature of the air entering.

• In the ZEITMOP-Separate cycle, the temperature of the mixture of carbon dioxide and oxygen exiting the OTM unit was the mass-averaged temperature of the oxygen entering (at the air temperature) and the carbon dioxide entering (at the carbon dioxide’s inlet temperature).

• In the ZEITMOP-Combined cycle, the temperature of the combustion gases exiting the OTM unit was the combustion temperature. The enthalpy value of the oxygen entering the combustion process was based on the air temperature.

• Some values were iteratively calculated.
The ZEITMOP-Separate cycle was simulated at a combustion temperature of 1400°C and a combustion pressure of 15 bar. These values were chosen based on previously published work on the ZEITMOP-Separate cycle, described in Section 2.5. When the ZEITMOP-Separate cycle was simulated using this method, the maximum temperature in the OTM unit was 841°C. However, the average temperature of the OTM unit, i.e. the mass-averaged temperature of the fluid in the OTM, was only 514°C. This is an extremely low operating temperature for an OTM, and so a second ZEITMOP-Separate cycle was simulated, in which a portion of the CO₂ was heated before entry to the OTM unit, in order to simulate a more realistic average temperature of 700°C in the OTM.

The ZEITMOP-Combined cycle was simulated at a combustion pressure of 15 bar and combustion temperatures of 1000°C (which would be the likely maximum combustion temperature if a perovskite membrane were used) and 1400°C.

The results of the calculations are presented in Section 7.1.

5.1.2. Initial Thermodynamic Calculations on the Efficiency of the OFFCET Cycle

Initial calculations on the OFFCET-Combined cycle were performed using the same simplifications and assumptions as were applied to the various combustion system options for the ZEITMOP plant, in addition to the assumptions below. The results should therefore not be considered as realistic, but should be comparable to the initial results for the ZEITMOP cycle. The additional assumptions and method of calculation are listed below.
• The fuel cell is assumed to be a “block” operating at steady state. Recirculation, reforming, control of temperatures in the cell, mixing of methane with steam (through recirculation of anode gases) etc. are all internal to the fuel cell “block”.
• Air and fuel can be delivered to the SOFC block at any temperature, and the maximum temperature in the cell is the anode exit temperature of 1000°C.
• The air stream exits the cell at 15°C below this temperature.
• The OTM is assumed to allow heat transfer in the same way as a heat exchanger, with a pinch point of 15°C.
• The energy produced by the conversion of some of the methane to products is easily calculated from the reaction energy using basic chemistry. It is assumed that all of this energy, minus the electrical power produced by the cell (voltage times current), is used to increase the temperatures of the gas streams. In this way the air flow rate required to keep the maximum temperature below 1000°C is calculated.
• Based on figures given by Kuchonthara et al.\textsuperscript{71} the conversion of methane is considered to be 85%, with 85% of that methane converted to CO\textsubscript{2} and H\textsubscript{2}O. The overall equation assumed to occur at the anode is therefore Equation 6.

\[
\text{CH}_4 + 1.5725\text{O}_2 \rightarrow \\
0.15\text{CH}_4 + 0.765\text{CO}_2 + 1.53\text{H}_2\text{O} + 0.085\text{CO} + 0.17\text{H}_2 + 620 \text{MJ/kmol}
\]

Equation 6: Assumed Reaction at SOFC Anode

The current in the fuel cell is directly related to the flow rate of oxygen, and is easily calculated as 4 mols of electrons travel through the outer circuit for each mol of oxygen, and the charge on one mol of electrons is Faraday’s constant. Based on the
equation shown above, the current is therefore 607 MA per kmol/s of methane. This is multiplied by the voltage to find the amount of energy removed from the system per kmol methane as electrical work. The rest of the energy of reaction (620MJ – Electrical work) is available to increase the temperatures of the anode and cathode gases. It is therefore a simple matter to calculate the excess air required to keep the temperatures of these two gas streams at the required levels.

The voltage was initially assumed to be 0.61 V, based on a detailed simulation of a SOFC operating directly on methane\(^4^9\). However in that simulation the flow rate of air was 4.43 times the stoichiometric amount. In the calculations for the OFFCET-Combined cycle the flow rate of air was calculated to be only 1.4 times the stoichiometric amount of air. The change in the Nernst voltage (i.e. the Nernst Potential) as a result of this difference can be calculated, so assuming the actual voltage is the Nernst voltage minus losses, the actual voltage can be recalculated and was found to converge at 0.604 V for this simplified model.

- The voltage in the calculations presented here is therefore 0.604 V.

The results of the calculations are presented in Section 7.2.

5.2. AspenPlus Simulations

The ZEITMOP-Combined cycle was simulated using AspenPlus version 11.1, and the results were compared to previously published results of simulations of the ZEITMOP-Separate cycle. The OTM combustion unit was simulated using a simplified model combining some standard Aspen modules and a slightly improved version of an Excel file used by Warchol\(^1^5\). The effect of heat exchange between the combustion and air streams in the OTM unit was included in the OTM model for these ZEITMOP-Combined simulations.
A new model for the OTM unit, which more accurately reflects the real-life situation, was developed and the results obtained with it were compared to the results from the previous model. The ZEITMOP-Combined cycle was then modelled using this newer model, and the effect of heat transfer from the air stream to the CO₂ stream was investigated.

Results available for the ZEITMOP-Separate cycle are for combustion temperatures between 1200°C and 1500°C, and delivery pressures for CO₂ between 90 bar and 210 bar. For this research the ZEITMOP-Combined cycle was simulated at combustion temperatures between 900°C and 1500°C, and delivery pressures of CO₂ between 90 bar and 210 bar, and also for combustion pressures between 3 and 40 bar when CO₂ is delivered at 210 bar.

5.2.1. Assumptions

The assumptions used in the AspenPlus simulations were:

- The OTM unit can withstand total pressure differences in the region of 1.5 bar across the membrane.
- The OTM unit can withstand temperature differences in the region of 1300 K both across and/or along the membrane.
- 98% of CH₄ is converted to CO₂ and H₂O. No other gases appear in the products of combustion.
- Heat exchanger pinch points are 14–16 K.
- The Peng-Robinson-Boston-Mathias Equation of State was used to calculate the properties of CO₂ and mixtures of CO₂ and either H₂O or O₂, at all relevant points.
- Pressure losses in heat exchangers and coolers are 3% of inlet pressure.
• Pressure losses in separators are 1.5% of inlet pressure.
• The pressure losses in the OTM are 5% of inlet pressure.
• Compressor isentropic efficiencies are 85 - 87%.
• Turbine efficiency was adjusted for cooling flow as described at ECOS 2006\textsuperscript{12}. This corrects the isentropic efficiency of the turbine for a coolant flow stream taken from the CO\textsubscript{2} intermediate stage compressor, but without modeling the coolant flow itself. The isentropic efficiencies of the air and combustion product turbines therefore vary from 89.5\% at 900°C to 85\% at 1500°C. As the properties of the flow streams at the outlet are calculated based on the corrected isentropic efficiency, this simplification does not affect the efficiency by more than the reduction caused by the lower isentropic efficiency (i.e. the work is not “lost” as in the simplified Excel model).
• Heat is rejected at 30°C.
• The OTM removes 60\% of the available O\textsubscript{2} from the air.

These assumptions are in accordance with both the first and second laws of thermodynamics. Most of the assumptions are similar to those used previously to simulate the ZEITMOP-Separate cycle, in order to allow as direct a comparison as possible between the two cycles. The only unrealistic assumption is that of perfect combustion, which was maintained as it was assumed for the previous ZEITMOP-Separate cycle simulations, and should not significantly affect the operation of the OTM unit. The major difference in simulations between the two cycles is the method of modeling the OTM unit, as previously described.
5.2.2. ZEITMOP-Combined with Simplified OTM Model

The simplified OTM model makes use of modules available in the AspenPlus software. The unit comprises three modules, a combustion chamber, a multiple stream heat exchanger, and an Excel module (OTM in Figures 36 – 38) that splits the air stream into a pure oxygen stream and a depleted air stream. The membrane is assumed to be a perfect heat exchanger. The real-world situation shown in Figure 37 is therefore modeled as shown in Figure 38.
The following calculation demonstrates that the assumption that the OTM unit operates as a perfect heat exchanger is valid. To heat 1.34 kmol of O₂ and 13.1 kmol of N₂ from 927°C to 1400°C, 221.5 MJ is required. 2 kmol/s of O₂ must be transported through the membrane to burn 1 kmol/s of CH₄. If the flux of the membrane is 1.24 μmol/(cm² s), the area of the membrane required is 161 x 10³ m². Assuming a thermal conductivity of 12 W/mK (values for thermal conductivities of various perovskites between 10 and 30 W/mK were found)⁷²,⁷³, a thickness of 1 mm,
and a temperature difference of 15°C across the membrane (the actual temperature differences across the membrane are 517°C at one end and 0°C at the other), the maximum one-dimensional heat transfer is 28,980 MW, about 130 times the heat transfer required. If the flux were 18 μmol/(cm² s), the membrane area would be 11 x 10³ m² and the unit would be capable of transferring 9 times the required heat transfer. It is likely that the thickness of the membrane would be much less than 1 mm, so the maximum heat transfer would be even higher than that calculated here. The areas of the heat exchangers calculated at the same design point were between 9 x 10³ and 25 x 10³ m².

5.2.3. ZEITMOP-Combined with New OTM Model

A new OTM model was designed. The ZEITMOP-Combined cycle was simulated with and without heat transfer from the air stream to the CO₂ stream using this OTM model.

The new OTM model is an Excel module linked to AspenPlus that modelled the actual processes in the OTM unit (removal of O₂ from air, combustion, heat transfer to air stream) using the assumptions described in section 5.2.1. The flux of the OTM was initially assumed to be 1.24 μmol/(cm² s) and was iteratively corrected for temperature and partial pressure ratio using Equation 1. The membrane was assumed to be a thin-film membrane 0.17 mm thick supported on a porous membrane. The maximum possible heat transfer was calculated based on one-dimensional heat transfer through the membrane, using an assumed value of thermal conductivity of 12 W/mK. The heat released by combustion was compared to the possible heat transfer. In all cases it was found that the possible heat transfer was much larger than the heat released by combustion. In other words, the OTM module will operate as an almost
perfect heat exchanger, just as was previously assumed in the simplified model. For this reason the temperature of the oxygen-depleted air exiting the OTM unit is almost the same temperature as the combustion temperature. The values of flux and thickness do not affect the efficiency found by the simulation, and were used only to calculate the area and heat transfer through the membrane. The new OTM model was used in AspenPlus simulations of ZEITMOP-Combined with and without heat transfer from the air stream to the CO₂ stream.

In the simulation with heat transfer (Figure 39) the CO₂ stream (G-CO2-7) is heated by both the air stream (AIR-5) and the combustion products (E-PR-3) before it is expanded. The air (AIR-2) is heated by the combustion products (E-PR-2) before entry to the OTM unit.

![Figure 39: AspenPlus ZEITMOP-Combined Simulation using New OTM Model With Heat Transfer from Air Stream to CO₂ Stream](image)

<table>
<thead>
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<th>Air</th>
<th>Air/oxygen depleted air</th>
<th>G-CO2</th>
<th>Carbon dioxide</th>
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<td>Oxygen</td>
<td>HEX</td>
<td>Heat Exchanger</td>
</tr>
<tr>
<td>C</td>
<td>Cooler</td>
<td>MHE</td>
<td>Multi Heat Exchanger</td>
</tr>
<tr>
<td>CC</td>
<td>Combustion chamber</td>
<td>OTM</td>
<td>Oxygen Transport Membrane</td>
</tr>
<tr>
<td>D-CH4</td>
<td>Methane</td>
<td>S</td>
<td>Compressor</td>
</tr>
<tr>
<td>E-PR</td>
<td>Combustion products</td>
<td>SEP</td>
<td>Separator</td>
</tr>
<tr>
<td>F-H2O</td>
<td>Liquid water</td>
<td>T</td>
<td>Turbine</td>
</tr>
</tbody>
</table>

Figure 39: AspenPlus ZEITMOP-Combined Simulation using New OTM Model With Heat Transfer from Air Stream to CO₂ Stream
In the simulation without heat transfer (Figure 40) the air is not heated before entry to the OTM unit, because this would reduce the heat available to the CO₂ stream. The CO₂ (G-CO2-7) is heated only by the exhaust products (E-PR-2) and the air is cooled in a cooling tower (AIR-5) before exiting to atmosphere. This heat is available as low-temperature heat if the system is used as a Combined Heat and Power (CHP) plant. The temperature of this waste heat (AIR-4) varies from 299°C at 900°C, 30 bar combustion to 1033°C at 1500°C, 5 bar combustion.

**Figure 40: AspenPlus ZEITMOP-Combined Simulation using New OTM Model**

Without Heat Transfer from Air stream to CO₂ stream
6. Experimental Work

6.1. Rig Concept

The outside of an OTM tube is exposed to air. Methane and a diluting gas flow through the centre of the tube, which is at a high temperature. Oxygen travels through the walls of the tube and burns with the methane. The exhaust is analysed to assess the flow rate of oxygen.

In the ZEITMOP-Combined cycle, methane and CO₂ enter the OTM unit on the permeate side, and compressed air enters on the feed side. As the methane and CO₂ pass over the membrane, the methane is burned and the proportion of methane is reduced, while the proportion of CO₂ and H₂O increase, so that at the end of the membrane, there is no methane left. In a real world plant, these tubes would likely be more than a metre in length. The samples purchased were only 10-20 cm long, as shown in Figures 41 – 42. The black tubes are the perovskite, and the white are the YSZ.
As the tubes are so small, it would be useful to simulate the flux at various positions along the length of a real-world tube. Figure 43 demonstrates this.
The section being simulated has an inward flow containing CH₄, CO₂ and H₂O. While there will be some dissociation, for the main part the CO₂ and H₂O do not participate in the combustion, and can be considered inert gas. This inert gas is simulated in the experiments by a mixture of CO₂, H₂O and Ar, which is produced and heated by burning O₂ and CH₄ in the presence of Ar.

Figure 43: Simulation of Conditions at Various Points Along the Real-World Tube
At different points along the real-world tube the proportions of methane and inert gas are different. Different positions along the tube can be simulated by altering this proportion. Different combustion temperatures can be simulated by altering the proportion of Ar in the mixture. In this way, a wide range of temperatures and CH₄/inert ratios (i.e. positions along the real world tube) can be produced simply by controlling the flow rates of the three inlet gases. The gases also provide heating for the testpiece.
6.2. Rig Design

Figure 44: Experimental Rig
Parts list

1. Mass flow controller
2. Spark generator
3. Gasket
4. OTM tube
5. Thermocouple
6. Sampling chamber for exhaust gas analyzer
7. Flashback arrestor

Figure 44 shows the layout design of the final rig. A cylinder of methane with a 2-stage pressure regulator was connected via flexible tubing to a Sierra Smart-Trak mass flow controller. O₂, Ar and compressed air were available on tap in the welding department of Dublin Institute of Technology and were connected via flexible tubing to Sierra Smart-Trak mass flow controllers. All the mass flow controllers were controlled via software using a laptop computer. Flashback arrestors protected the methane and oxygen mass flow controllers. The methane, O₂ and Ar lines entered a cylindrical combustion chamber composed of alumina via metal inlet tubes. Two electrodes connected to a spark generator and a thermocouple protruded into the combustion chamber. The spark generator provided a continuous stream of sparks when turned on.
The combustion chamber, shown in Figure 45, was a closed-end alumina tube. An alumina plate with a hole in it was glued to the other end. A gasket separated this plate from the testpiece. An outer metal tube enclosed the testpiece, and was split into two parts, to allow for assembly and disassembly. Screwing the two parts together would allow for some flexibility in length, however when the testpiece is in place, screwing the outer tube closed would apply a rotational force to one end of the ceramic relative to the other. The solution was to use a connector that turned externally, while the two outer tube parts remained stationary. Three connectors were made, to allow for the different tube lengths.

The ends of the metal tubes were encased in very short ceramic tubes, one of which is glued to the combustion chamber end plate, the other to a second end plate,
which was glued to an alumina tube sized for the analysis equipment. The manufactured parts of the rig were designed in Solid Edge, as demonstrated by Figure 46.

Gaskets separated the testpiece from the end plates for extra protection from external forces and to compensate for any irregularities in the tube ends. When the outer tube was assembled, the gaskets were compressed, providing an air-tight seal. Calculations showed that the small increase in length caused by thermal expansion could be withstood by the gaskets alone.
Structural strength was added by steel beams linking the metal inlet tubes to the steel outer tube, clearly visible in Figure 47. Type K thermocouples capable of withstanding temperatures as high as 1335°C were purchased. The thermocouples had bright green wires, making them easily identifiable in Figure 48. A Picolog thermocouple reader logged the readings from the 6 thermocouples every second and stored them on the laptop computer. Figure 49 shows the entire rig, excepting the analysis equipment and computer.
6.3. Materials Used in Rig

All the parts that were in contact with the combustion gases i.e. the combustion chamber, combustion gas exhaust and end plates, were manufactured from alumina. Machining was performed by McGeoch Technology. The other manufactured parts were made from steel in the Dublin Institute of Technology, for ease of manufacture. Rather than glue the steel outer tube directly to the end plates, small alumina tubes were glued to the end plates and the steel tubes were fitted inside these. This ensured that if the steel expanded more than the ceramic, the glue would be compressed rather than sheared or pulled apart.

The flexible plastic tubing used could not be attached to the combustion chamber directly or it would melt. Metal tubes were glued into holes in the combustion chamber, and were of sufficient length that the plastic tubing attached to the other end did not melt. These tubes were also used to provide connection to the mass flow controllers, as shown in Figure 50. Brass was used for the oxygen and air lines, steel for the methane line, and both brass and steel in the Ar line.
Air tight connections were achieved with Ceramabond glue, capable of withstanding temperatures in excess of those envisaged. The parts were glued together and then the assemblies were cured in an oven. The gaskets were sourced from Kemtron and were capable of withstanding the combustion temperatures. Plumbers tape was used on the threaded parts of the rig to provide an airtight seal.

6.4. Analysis Equipment

A gas chromatograph was thought to be the best method of measuring the oxygen flux, however a suitable gas chromatograph proved difficult to source. A gas chromatograph equipped with a gas sampling valve was required to test gases as opposed to liquids. To test for the gas species expected in the exhaust, the gas chromatograph required a thermal conductivity detector, as opposed to the more common flame ionisation detectors. Finally Porapak Q material was required in the column, however this last was not problematic as the column material could be changed. It proved impossible to get access to a gas chromatograph of these specifications. In addition to this problem, a gas chromatograph takes about 15
minutes to process a sample, which must be a discrete sample taken manually using a
gas syringe. This would severely restrict the experiments. An online gas
chromatograph would be able to continuously sample a gas stream; however such a
machine is very expensive. Other methods of testing the outlet gas were investigated.

Vehicle emissions testing equipment, which was readily available in the
college, was for some time thought to be a viable alternative. The equipment gives
percentage readings for the various species expected in the outlet gas, and the results
are practically instantaneous, with digital output possible. However there are very few
manufacturers of vehicle emissions testers, and none publish any information on the
operation of the machines, other than to say that they meet relevant standards. It is
impossible to tell which species are measured and which calculated based on the
assumption that the fuel is burned in air, an assumption that certainly does not apply to
this rig.

The solution decided on was another type of commercially available analyzer:
an exhaust gas analyzer, used to test exhausts from burners of all kinds. The top of the
range models test for all required species, rather calculating results based on the
assumption of combustion in air. The analyzer had the advantage of taking one
reading per second, allowing many more results to be taken in a shorter time, and
came equipped with software to export results to the laptop computer. These
advantages, combined with a price tag less than half that of a gas chromatograph, led
to the choice of a Testo 350 exhaust gas analyzer as the equipment for the rig. The
exhaust gas analyzer probe had an immersion depth of 300 mm and a diameter of 15
mm, so the combustion and air exhausts of the rig were hollow tubes of 30 mm
internal diameter, 350 mm in length. This allowed measurements to be taken for the outlets of both the fuel and air streams. The Testo probe can be seen in the foreground of Figure 51.

![Figure 51: Flame in Combustion Chamber](image)

Two thermocouples are also visible, one extending from within the combustion chamber through the end plate (T2), and the other protruding through the wall of the steel tube (T3). The first would be used to measure the temperature inside the testpiece and the second to measure the temperature outside the testpiece. A similar arrangement existed at the other end of the testpiece (T5 and T6). The temperature of the combustion (T1) and the temperature outside the testpiece, midway along its length (T4) were also measured. The Testo equipment measured the temperature of the analysed gas stream.
The connection visible on the right hand side of the metal tube is the air inlet. This was not glued to the rig, but could be disassembled, to allow for both coflow and counterflow arrangements.

6.5. Safety

The rig used pressurised flammable gases and incomplete combustion was likely to occur. Therefore there were a number of safety standards to be met. By conducting the experiments in the Welding Department of the Dublin Institute of Technology, most of these standards were easily achieved. Gas was supplied safely in the department, and the exhaust could be safely disposed of. A transparent screen, shown in Figure 52, was placed in front of the rig and the researcher wore protective goggles.

Figure 52: Protective Screen


6.6. Experiments Performed

6.6.1. Explosive Combustion

The rig was assembled and the Testo probe was placed in the combustion exhaust chamber. The oxygen flow rate was set to 0.8 standard litres per minute (slpm), and the methane flow rate to 0.4 standard litres per minute, which is the stoichiometric amount of fuel for that oxygen flow rate. These flowrates had previously achieved steady state combustion in the rig when the spark generator was switched on prior to the methane beginning to flow. However the spark generator was not switched on before the methane began to flow for this test.

The correct procedure would have been to stop the methane flow, wait for a short period, switch on the spark generator, and then start the methane flow. However, due to human error the spark generator was switched on while the methane was flowing. This led to an explosion that broke the exhaust chamber, as shown in Figure 53. Temperature and exhaust gas data were collected during this failed test.

6.6.2. Steady State Combustion Without a Testpiece

The rig was assembled without a testpiece. The Testo probe was placed into the broken end of the exhaust chamber, as shown in Figure 54. The damage to the

Figure 53: Damage to Exhaust Chamber

Figure 54: Damage to Exhaust Chamber
exhaust chamber meant that the Testo probe measured ambient air mixed with the exhaust gases.

Figure 54: Use of Testo Analyzer Without Exhaust Chamber

The flow rate of oxygen was set to 0.8 slpm and the spark generator was turned on. The flow rate of methane was set to 0.4 slpm. On the first spark after the methane began to flow the combustion started with a loud bang. Steady-state combustion was achieved and temperature and exhaust gas data were collected. The gas flow rates were increased in stages as follows. The oxygen flow rate was increased to 1 slpm, then the methane flow rate was increased to 0.5 slpm. The delay between these increases was less than a second. The new flow rates were maintained for about 40 seconds. The procedure was then repeated. Ar was then introduced to the mix. Next the oxygen flow was increased, but the methane was not increased for about 35 seconds. Finally the methane was increased to the stoichiometric level. The Testo probe was then removed from the combustion gas stream and placed in the air exhaust. The PicoLog reader automatically stopped taking samples. After about 50 seconds the probe was returned to the exhaust stream. The methane flow rate was set to 0, the oxygen flow
rate was set to 0 and the Testo was stopped. The steady state combustion is visible in Figure 55.

Figure 55: Combustion Chamber Glowing Red Hot in the Vicinity of the Steady Flame

6.6.3. Steady State Combustion With a Testpiece

After the rig had cooled sufficiently it was disassembled and reassembled with a testpiece in situ. The same startup procedure and initial flow rates were used, however the combustion did not begin on the first spark. After a few sparks the combustion began with an extremely loud bang. Steady-state combustion was achieved and temperature and exhaust gas data were collected.

During the test steam was visible exiting the air exhaust so it was obvious that the testpiece had broken. The Testo probe was removed from the combustion exhaust stream and inserted in the air exhaust. After a period of time it was replaced in the exhaust gas stream. Towards the end of the test water dripped continually out of the rig, so it was obvious that the rig was no longer airtight. The gas flow rates were not increased to the same level as in the previous test. The maximum combustion temperature achieved was about 600°C.
After the rig was disassembled it was found that the testpiece had shattered. The end plate had also been forced away from the outer tube and was loose. The damage is shown in Figures 56 – 57.

Figure 56: Shattered Testpiece

Figure 57: Gap Between End Plate and Outer Tube
6.6.4. Steady State Combustion Without Outer Tube Assembled

Data was collected for steady state combustion without the outer tube assembled. The outlet of the combustion chamber was open to air, as shown in Figure 58.

![Figure 58: Analysis of Combustion Chamber Outlet Gases](image)

6.7. Analysis of OTM Microstructure

Samples of both membrane materials were analysed using an Atomic Force Microscope, shown in Figure 59. The microstructure and grain size were clearly visible.

![Figure 59: Atomic Force Microscope](image)
6.8. Future Use

The rig developed during the current research may be used for future research into the ZEITMOP and OFFCET cycles, or for research into other uses for OTMs. In order to ensure that explosive combustion does not occur again, a pilot light, rather than a spark generator, is required. The microscopic analysis of the membrane samples may be used to assess changes in the microstructure following future experimentation.
7. Results and Discussion

Results are presented here for the initial excel calculations on the ZEITMOP cycle and the AspenPlus simulations of the ZEITMOP-Combined cycle using both OTM models. The results are compared to previously published research on the ZEITMOP-Separate cycle. The results of the initial Excel calculations on the OFFCET cycle are discussed. Results of the limited experimental work completed are also presented.

7.1. Results of Initial Calculations on ZEITMOP

7.1.1. ZEITMOP-Separate

Results for the ZEITMOP-Separate using these assumptions are shown in Table 7. The node points are the same as those in Figure 60, which is identical to Figure 8.

![Figure 60: ZEITMOP-Separate](image)

The simplified assumptions have resulted in an efficiency of 51%, which is similar to the 50% efficiency found by the AspenPlus simulation described in section 2.5.
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Table 7: Calculations for ZEITMOP-Separate
7.1.2. ZEITMOP-Separate with Higher OTM Operating Temperature

The average temperature in the simulated OTM was increased by heating some of the CO$_2$ before entry to the OTM. The CO$_2$ stream splits at point 16. Some of the CO$_2$ enters the combustion chamber directly, while the rest is heated by the hot exhaust products before entering the OTM. The portion of CO$_2$ that enters the heat exchanger is chosen to ensure an average temperature of 700ºC in the OTM. This change in layout is illustrated in Figure 61. The results of the calculations for this layout are shown in Table 8. Temperature – specific entropy and pressure – specific volume diagrams were also generated for this cycle, and are shown in Figures 62-63. The node points in Table 8 and Figures 62-63 are the same as in Figure 61.

![Figure 61: ZEITMOP-Separate with Higher OTM Operating Temperature](image-url)
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<th>(P)</th>
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<td>([\text{kg/s}])</td>
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Table 8: Calculations for ZEITMOP-Separate with OTM Unit Operating at an Average Temperature of 700ºC
Figure 62: Temperature-specific entropy diagram for ZEITMOP-Separate

Figure 63: Pressure – specific volume diagram for ZEITMOP-Separate
As can be seen from these calculations, the efficiency is slightly increased to 52% by the increase in the CO$_2$ temperature before combustion. This is due to the larger mass of CO$_2$ that is required to keep the combustion temperature below 1400ºC. Unfortunately the temperature at node 5 is severely reduced, leading to a corresponding reduction in temperature at node 15, and hence a reduction in the work produced by the high pressure CO$_2$ turbine. This means that less work is generated by expanding the CO$_2$ than is used to compress it. Removing the CO$_2$ turbine only results in further loss of efficiency, as compression of the recirculated CO$_2$ to the combustion pressure is still necessary, and the turbine allows at least some of this work to be reclaimed.

Reducing the maximum temperature of the air stream would reduce the work done by the air turbine, but increase the work done by the CO$_2$ turbine. Regardless of the effect on the efficiency, there is an advantage to ensuring that the CO$_2$ turbine can power the CO$_2$ compressor: the system is easier to design from a mechanical point of view. The average temperature of the OTM is 700ºC and the natural log of the average oxygen partial pressure ratio is 0.416.

### 7.1.3. ZEITMOP-Combined at Low Combustion Temperature

The temperature at which the combustion occurs will be determined by the limits of the OTM material. At present the maximum temperatures most perovskite materials can withstand is 1000ºC. Calculations for ZEITMOP-Combined with a combustion temperature of 1000ºC are shown in Table 9. The node points are the same as those in Figure 64, which is identical to Figure 35. Reducing the combustion temperature results in a severe drop in efficiency.
Figure 64: ZEITMOP-Combined

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<th>P</th>
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Table 9: Calculations for ZEITMOP-Combined With a Combustion Temperature of 1000°C

7.1.4. ZEITMOP-Combined at High Combustion Temperature

<table>
<thead>
<tr>
<th>node</th>
<th>fluid</th>
<th>n [kmol/s]</th>
<th>m [kg/s]</th>
<th>P [bar]</th>
<th>V [m³/s]</th>
<th>T [K]</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₄</td>
<td>1.0</td>
<td>16</td>
<td>1</td>
<td>24.0</td>
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<td>15</td>
</tr>
<tr>
<td>2</td>
<td>CH₄</td>
<td>1.0</td>
<td>16</td>
<td>15</td>
<td>2.79</td>
<td>504</td>
<td>231</td>
</tr>
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<td>3</td>
<td>CO₂&amp;H₂O</td>
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<td>780</td>
<td>15</td>
<td>175</td>
<td>1673</td>
<td>1400</td>
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<td>CO₂&amp;H₂O</td>
<td>18.9</td>
<td>780</td>
<td>1</td>
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<td>1129</td>
<td>856</td>
</tr>
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<td>780</td>
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<td>CO₂&amp;H₂O</td>
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<td>780</td>
<td>1</td>
<td>731</td>
<td>465</td>
<td>192</td>
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<tr>
<td>7</td>
<td>CO₂&amp;H₂O(l)</td>
<td>18.9</td>
<td>780</td>
<td>1</td>
<td>426</td>
<td>303</td>
<td>30</td>
</tr>
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<td>8</td>
<td>CO₂</td>
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<td>744</td>
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<td>426</td>
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<td>744</td>
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<td>CO₂</td>
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<td>13</td>
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<td>744</td>
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<td>2.63</td>
<td>393</td>
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<td>700</td>
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<td>700</td>
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<tr>
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<td>1</td>
<td>0.036</td>
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<td>30</td>
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<td>1.0</td>
<td>44</td>
<td>210</td>
<td>0.16</td>
<td>393</td>
<td>120</td>
</tr>
<tr>
<td>20</td>
<td>Air</td>
<td>10.5</td>
<td>304</td>
<td>1</td>
<td>251</td>
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<td>15</td>
<td>64.7</td>
<td>1114</td>
<td>841</td>
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<td>23</td>
<td>N₂&amp;O₂</td>
<td>8.5</td>
<td>240</td>
<td>15</td>
<td>52.3</td>
<td>1114</td>
<td>841</td>
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<td>24</td>
<td>N₂&amp;O₂</td>
<td>8.5</td>
<td>240</td>
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<td>362</td>
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<td>15</td>
<td>12.3</td>
<td>1114</td>
<td>841</td>
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### Table 10: Calculations for ZEITMOP-Combined With a Combustion Temperature of 1400°C

<table>
<thead>
<tr>
<th>Process</th>
<th>[MW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ compression</td>
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<td>Exhaust expansion</td>
<td>453</td>
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<tr>
<td>CO₂ compression</td>
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<td>CO₂ expansion</td>
<td>212</td>
</tr>
<tr>
<td>Air compression</td>
<td>-86</td>
</tr>
<tr>
<td>Air expansion</td>
<td>95</td>
</tr>
<tr>
<td>Total work</td>
<td>406</td>
</tr>
<tr>
<td>LHV CH₄ [MJ/kmol]</td>
<td>800</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>51%</td>
</tr>
</tbody>
</table>

Table 10 shows the results of the calculations for ZEIMOP-combined with a combustion temperature of 1400°C. A fluorite membrane OTM unit would be required for this operating temperature. By increasing the combustion temperature to the original 1400°C, the efficiency has been returned to its original value of 51%. Many of the other parameters are also identical to the original cycle, e.g. the quantity of recirculating CO₂.

#### 7.1.5. Comparison of ZEITMOP-Separate and ZEITMOP-Combined

The results of the initial Excel calculations implied that at high combustion temperatures the efficiency of the ZEITMOP-Combined cycle is similar to the efficiency of the ZEITMOP-Separate cycle, but that the combined option at low combustion temperatures has a lower efficiency than the efficiency of either option at higher combustion temperatures. In other words, the combined option was found to be worthwhile only if the OTM/combustion unit can operate at high temperatures.
The highest efficiency for all the options investigated using the Excel model resulted from heating the CO₂ before entry to the combustion chamber. This is one of the reasons that the effect of heat transfer to the CO₂ stream was studied using AspenPlus.

7.2. Results of Initial calculations on OFFCET

The results of the initial thermodynamic calculations on the OFFCET-Combined cycle are presented in Table 11. The efficiency is 61.2%. Temperature – specific entropy and Pressure – specific volume diagrams were generated and are shown in Figures 66-67. The node points are the same as in Figure 65, which is identical to Figure 29.

Figure 65: OFFCET- Combined
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1000</td>
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<td>393</td>
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<td>35.33</td>
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<tr>
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<td>CO₂</td>
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<td>44</td>
<td>210</td>
<td>0.16</td>
<td>393</td>
<td>120</td>
</tr>
<tr>
<td>15</td>
<td>H₂O (l)</td>
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<td>36</td>
<td>1</td>
<td>0.036</td>
<td>303</td>
<td>30</td>
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<tr>
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<td>Air</td>
<td>13.5</td>
<td>392</td>
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<td>324</td>
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<td>Air</td>
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<td>535</td>
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<td>565</td>
<td>591</td>
<td>318</td>
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<td>O₂</td>
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<td>10</td>
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<td>Power [MW]</td>
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<table>
<thead>
<tr>
<th>Process</th>
<th>[MW]</th>
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<tbody>
<tr>
<td>CH₄ expansion</td>
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<tr>
<td>Exhaust expansion</td>
<td>59</td>
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<td>CO₂ compression</td>
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<td>Air compression</td>
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<tr>
<td>Air expansion</td>
<td>162</td>
</tr>
<tr>
<td>Total work</td>
<td>128</td>
</tr>
</tbody>
</table>

| LHV CH₄ [MJ/kmol] | 807  |
| Thermal efficiency | 61.2% |

Table 11: Calculations for OFFCET-Combined
Figure 66: Temperature-specific entropy diagram for OFFCET-Combined

Figure 67: Pressure – specific volume diagram for OFFCET-Combined
Methane is delivered at 30 bar to the OFFCET cycle, and at 1 bar to the ZEITMOP cycle. The figure of 30 bar was decided upon following discussions with Bord Gais, who supply natural gas to power plants in Ireland at 30 bar. This means that an extra 8.14 MW of energy per kmol of methane enter the system. To compare the OFFCET cycle with the ZEITMOP cycle, an efficiency of 60.2% should be used. This is significantly higher than the efficiency of the ZEITMOP cycle calculated in a similar manner, however there was another difference. The OTM unit in the OFFCET initial calculations was assumed to operate as a heat exchanger and that in the ZEITMOP cycle was not. This heat transfer can be seen in Figure 66, show as the arrow between 4-5 and 22-26. The effect of this heat transfer is to increase the temperature of the air at inlet to the air turbine, and therefore to increase the efficiency of the air cycle. However it can be seen that this represents a small fraction of the energy transfers in the cycle, so it is likely that the OFFCET-Combined cycle would have a higher efficiency than the ZEITMOP cycle. The results of these initial calculations imply that the OFFCET cycle warrants further investigation.
7.3. Results of AspenPlus Simulations of the ZEITMOP-Combined Cycle Using the Simplified OTM Model

As can be seen in Figure 68, at temperatures of 1150°C and above, the highest efficiency is found for combustion pressures in the region of 3-5 bar. The slopes for these two pressure levels are almost identical, with the 5 bar values slightly higher at high temperatures.

The efficiency varies much more with combustion temperature than with combustion pressure. The efficiency rises with temperature for all combustion pressures. At relatively low combustion pressures (3 to 10 bar) the efficiency rises smoothly with temperature. At 40 bar there is a different shape to the curve, with a
sharper increase in efficiency at lower temperatures, and a lower slope at higher temperatures.

At intermediate combustion pressures (15 to 30 bar) there are two distinct regions in the efficiency/temperature curve. At lower temperatures the curve resembles the high-pressure curve, while at higher temperatures the curve resembles the low-pressure curve. By analysis of the temperatures of individual streams, it was found that this is related to the operation of the multi-stream heat exchanger, (MHE2 in Figure 36). This transfers heat from both the depleted air stream (AIR-6) and the combustion products stream (E-PR-3) to the recirculated CO\textsubscript{2} stream (G-CO2-7). At lower combustion temperatures (below 1000°C for 15 bar, 1100°C for 20 bar and 1300°C for 30 bar), E-PR3 is hotter than Air-6 at the inlet to MHE2, whereas at higher combustion temperatures, Air-6 is hotter than E-PR3. As the temperature of the CO\textsubscript{2} stream depends on the hotter of the two feed streams, the power output of the CO\textsubscript{2} turbine is directly affected by this change. This result is one of the reasons that the effect of heat transfer from the air stream to the CO\textsubscript{2} stream was studied in more detail in the next set of simulations.

On close inspection the results of these simulations show that the improvement in efficiency resulting from the heat transfer from air to CO\textsubscript{2} depends on the pressure to which the air is compressed before entry to the OTM unit; at high pressure ratios the waste heat from the exit of the air turbine is not suitable to heat the CO\textsubscript{2} stream. As OTMs are ceramic the total pressure on both sides was assumed to be as close to identical as possible, so that the pressure to which the air is compressed is similar to the combustion pressure. The highest efficiency was found for combustion pressures of 3-5 bar, at which pressures the heat exchanger transfers useful heat from the air stream to the CO\textsubscript{2} stream. The different slopes in the efficiency/temperature curve
depend on the use of this heat exchanger. When heat is not transferred from air to CO₂, the efficiency has a maximum, and the curve levels off. However when the waste heat from the air stream is transferred to the CO₂, the efficiency continues to rise with temperature up to the highest temperature investigated (1500°C). In the next set of simulations results are presented for the combined cycle with and without this heat transfer for combustion pressures from 5 – 30 bar.

A second reason for the change in slopes is that the temperature of combustion directly affects the amount of CO₂ recirculated in the system, as the CO₂ acts as coolant for the combustion chamber. This difference is more pronounced at lower temperatures and pressures (resulting in steeper slopes of the curve). Both of these effects directly affect the power produced by the CO₂ turbine, and hence the efficiency.

Figure 69: Efficiency of ZEITMOP-Combined at a Combustion Pressure of 15 bar
Figure 69 demonstrates that the efficiency rises smoothly as CO₂ delivery pressure drops. This is because less work is required to compress the CO₂. In a carbon capture and storage situation, the CO₂ would be sequestered and would need to be at a particular pressure depending on the sequestration site. If the cycle delivers liquid CO₂ at a pressure lower than this, it would need to be compressed again. For optimal efficiency the cycle should be operated at the minimum CO₂ delivery pressure that is suitable for the chosen sequestration option. Compressors for enhanced natural gas recovery which compress CO₂ to 190 bar are commercially available implying that the required CO₂ delivery pressure is likely to be in the range of 180 to 210 bar, depending on a particular gas well or other sequestration option.

![Comparison of ZEITMOP-separate and ZEITMOP-combined](image)

Figure 70: Efficiencies of ZEITMOP-Separate and ZEITMOP-Combined
Figure 70 compares the efficiency of ZEITMOP-Combined to previously published research on the ZEITMOP cycle. The values in Figure 70 are for a combustion pressure of 15 bar and a CO₂ delivery pressure of 210 bar. It seems that the combined ZEITMOP cycle is more efficient than the separate ZEITMOP cycle at temperatures above 1200°C. Most likely below this temperature both cycles have a lower efficiency. As the Graz group designed a majority CO₂ turbine that can operate at 1300°C, it seems unlikely that the ZEITMOP plant would ever be built with a combustion temperature lower than 1200°C. In other words, ZEITMOP-Combined is only feasible with an OTM unit operating at temperatures above 1200°C. A lower-temperature membrane unit would only be suitable for the ZEITMOP-Separate cycle.

The efficiency of the ZEITMOP-Separate cycle with heat transfer from the air stream to the CO₂ stream was only calculated in one case – at 1200°C and 90 bar delivery pressure – and was found to be 7% higher than the cycle without heat transfer. The efficiency was assumed to be 7% higher in all cases. This assumption is valid for the cycle at 1200°C and 210 bar, as the efficiency falls steadily with rising CO₂ delivery pressure.

7.4. Results of AspenPlus Simulations of the ZEITMOP-Combined Cycle Using the New OTM Model

7.4.1. Comparison of Simplified and New models

It is obvious from Figure 71 that the two models give very similar results, implying that the Excel model based on physical processes is equally as valid as the simplified model using AspenPlus modules, and vice versa. Simulations were
performed using the new model at combustion temperatures from 900°C – 1500°C and combustion pressures from 5 – 30 bar.

![Efficiency vs Temperature](image)

**Figure 71:** Efficiency of ZEITMOP-Combined Simulated Using the Simplified and New OTM Models

### 7.4.2. Sample results of Individual Simulations

In total, 111 AspenPlus simulations were performed. Properties of the fluid at node points and work consumed or produced during various processes are shown in Tables 12 and 13 for two sample simulations. These are the simulations of the ZEITMOP-Combined cycle with heat transfer from air to CO₂, at a combustion pressure of 15 bar, and combustion temperatures of 1000°C and 1400°C. The node points are the same as in Figure 72, which is identical to Figure 39. Temperature – specific entropy and pressure – specific volume diagrams were also generated for this cycle, and are shown in Figures 73 - 74.

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Figure 72: The AspenPlus Simulation used to produce Tables 12 and 13

<table>
<thead>
<tr>
<th>Stream</th>
<th>[kmol/s]</th>
<th>[kg/s]</th>
<th>[bar]</th>
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<td>380.805</td>
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Table 12: Values at node points of AspenPlus Simulation of ZEITMOP-Combined Cycle with Heat Transfer from Air to CO₂, at a Combustion Pressure of 15 bar, and a Combustion Temperature of 1000°C

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<th>( m ) [kg/s]</th>
<th>( P ) [bar]</th>
<th>( V ) [m³/s]</th>
<th>( T ) [°C]</th>
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<td>458.772</td>
<td>1.000</td>
<td>380.805</td>
<td>15.000</td>
</tr>
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<td>341.159</td>
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Table 13: Values at Node Points of AspenPlus Simulation of ZEITMOP-Combined Cycle with Heat Transfer from Air to CO2, at a Combustion Pressure of 15 bar, and a Combustion Temperature of 1400°C

Figure 73: Temperature – specific entropy diagram for ZEITMOP-Combined Cycle with Heat Transfer from Air to CO2, at a Combustion Pressure of 15 bar, and a Combustion Temperature of 1400°C
The proportions of the gas species in the flow exiting the combustion chamber were calculated for three of the simulations of ZEITMOP-Combined with heat transfer using the new model. At a combustion temperature of 1300°C and a combustion pressure of 30 bar the flow contains 81% CO₂ and 19% H₂O by mass. At 1300°C and 5 bar it contains 86% CO₂ and 14% H₂O, and at 1500°C and 5 bar it contains 83% CO₂ and 14% H₂O by mass.
7.4.3. Efficiency of ZEITMOP-Combined Cycle Without Heat Transfer from Air to CO₂

Figure 75 shows the results of the AspenPlus simulations of the ZEITMOP-Combined cycle without heat transfer from air to CO₂ using the new OTM model. The delivery pressure of CO₂ was 210 bar and the different curves represent different combustion pressures. Without the heat transfer, the waste heat leaving the air turbine is not used in the cycle. At high combustion temperatures and low combustion pressures this heat is a major loss. The efficiency has a maximum of between 1200°C and 1300°C and rises steadily with combustion pressure.

The possibility of not using a heat exchanger, even at high combustion temperatures, should not be disregarded because with the absence of the heat transfer...
the air leaving the air turbine is at a high temperature, suitable for heating. A CHP ZEITMOP plant would be particularly useful for any industrial process requiring CO₂.

7.4.4. Efficiency of ZEITMOP-Combined Cycle With Heat Transfer from Air to CO₂

Figure 76: Efficiency of ZEITMOP-Combined With Heat Transfer from Air to CO₂

Figure 76 shows the results of the AspenPlus simulations of the ZEITMOP-Combined cycle with heat transfer from air to CO₂ using the new OTM model. At high combustion pressures and low combustion temperatures the additional heat exchanger has very little effect. Therefore at high pressures and low temperatures the efficiencies are similar for the cycle with and without heat transfer. At higher combustion temperatures and low pressures the heat exchanger vastly increases efficiency. The efficiency rises steadily with temperature when the heat transfer is
useful, but is similar to the curve in Figure 75 when the heat exchange is not useful. The slope of the curve changes sharply when the heat transfer becomes useful.

There are two curve shapes – with and without heat transfer. The curve switches at different temperatures for each combustion pressure. At 5 bar, the heat transfer is useful at all temperatures so it rises smoothly. At 30 bar, the heat transfer only becomes useful above 1300°C so the curve switches from the no-heat-transfer curve to the heat-transfer curve at this point. For 20 bar and 15 bar the curve switches somewhere between 1100°C and 1300°C.

### 7.5. Comparison of ZEITMOP Options

Figure 77 compares the most recent results for the various ZEITMOP options at 15 bar combustion pressure. The values for the ZEITMOP-Separate with heat transfer from air to CO₂ (dotted line) were calculated assuming an increase of 7% at all temperatures. This assumption is valid at 1200°C.

**Figure 77: Comparison of Different Options for ZEITMOP Cycle**
At combustion temperatures above 1200°C the transfer of heat from the air to the CO₂ stream improves the efficiency of the ZEITMOP-Combined cycle. The improvement is more pronounced at higher combustion temperatures. This indicates that the assumption that the efficiency of the ZEITMOP-Separate is increased by the same amount at all combustion temperatures is invalid. At 1200°C, the efficiency of the ZEITMOP-Separate and ZEITMOP-Combined are almost identical. The ZEITMOP-Separate cycle with heat transfer may or may not be as efficient as the ZEITMOP-Combined cycle above 1200°C.

7.6. Exergetic Evaluation of OTM Unit

Exergy is the maximum amount of work that can be obtained from a substance by bringing it to the state of the surroundings. The exergy of a substance within a flow stream, shown in Equation 7, is the work and heat that can be obtained by bringing the substance to the reference state, shown in Table 14, plus the chemical exergy of the substance.

\[ \varepsilon = w_{\text{isentropic\_expansion\_to\_reference\_pressure}} + q_{\text{cooling\_to\_reference\_temperature}} + \mu \]

- \( \varepsilon \) Specific exergy
- \( w \) Specific work
- \( q \) Specific heat transfer
- \( \mu \) Specific chemical exergy

Equation 7: Exergy of a substance within a flow stream
The exergetic efficiency, or second law efficiency, of a thermodynamic unit is shown in Equation 8.

\[
\eta = \frac{\varepsilon_{\text{out}}}{\varepsilon_{\text{in}}}
\]

\[
\eta \quad \text{Exergetic efficiency}
\]

\[
\varepsilon \quad \text{Exergy}
\]

Equation 8: Exergetic efficiency of a thermodynamic unit

An exergetic analysis of the OTM combustion chamber in ZETIMOP-Combined was performed at a combustion temperature of 1400°C and a combustion pressure of 15 bar. The isentropic work of expansion to the reference pressure was found for each substance using Equation 5, with \(P_1\) and \(V_1\) being the actual pressure and volume of 1 kg of the substance and \(P_2\) and \(V_2\) being the pressure and volume at the reference state. The volume at the reference state was calculated using the ideal gas law. The heat obtained by cooling to reference temperature was found using the specific heat capacity of the substance averaged between the actual temperature and the reference temperature.

The values used for the calculation are shown in Table 15. The exergetic efficiency of the OTM unit is 69.8%.

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Table 14: Reference Environment for Exergetic Analysis
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<th>q [kJ/kg]</th>
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<th>ε [MW]</th>
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<td>130</td>
<td>658</td>
<td>52142</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
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<td></td>
<td>348</td>
<td>392</td>
<td></td>
<td>-201</td>
<td></td>
</tr>
<tr>
<td>E-PR-1</td>
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<td>1674</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CO2</td>
<td>11.64</td>
<td></td>
<td>392</td>
<td>992</td>
<td></td>
<td>-119</td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>2.61</td>
<td></td>
<td>35.9</td>
<td>1565</td>
<td></td>
<td>481</td>
<td></td>
</tr>
</tbody>
</table>

Table 15: Exergetic Evaluation of OTM Unit at a Combustion Pressure of 15 bar, and a Combustion Temperature of 1400°C

7.7. Comparison of ZEITMOP-Combined With State of the Art Combined Cycles

The most efficient combined cycle in existence today, GE’s H-turbine plant, claims a thermal efficiency of about 60% at a turbine inlet temperature of 1430°C\(^75\). This is higher than the highest thermal efficiency of the ZEITMOP cycle at this temperature, which is about 49%. The high efficiency of this cycle is achieved using closed loop steam cooling, in which steam used to cool the turbine blades is used in a steam cycle.

Based on values in Table 13, the energy lost as heat transfer in the turbines is of the order of 27% of the lower heating value of the methane. If this heat were transferred to a steam cycle with a thermal efficiency of 41%, the ZEITMOP-
Combined cycle could reach an efficiency equal to the GE cycle. The GE cycle does not capture the carbon dioxide it produces into the atmosphere.

The OTM unit is so deeply integrated with the ZEITMOP cycle that it does not make sense to calculate the loss of efficiency due to production of oxygen. However, other work published by other authors show an increase in efficiency of 1.04% to 3% and a reduction in capital cost of 25% when comparing cycles using OTMs to those using other methods of oxygen production.\textsuperscript{76,77}

7.8. Experimental Results

The data collected from the thermocouple reader and the Testo Gas Analyzer are presented for the four tests described in section 6.6. The Atomic Force Microscopic analysis of the membrane samples is also presented. The Testo analyzer measured a large number of gas species and other values. Selected results are displayed graphically and relevant results are discussed. Both the Picolog thermocouple reader and the Testo analyzer recorded data once a second.

The thermocouple positions were as follows: T1 measured the combustion temperature. T2 was positioned just outside the exit of the combustion chamber, to measure the temperature inside the testpiece at the combustion end. T3 measured the temperature outside the testpiece at the combustion end. T4 protruded through the outer tube connector and measured the temperature outside the testpiece, midway along its length. T5 measured the temperature outside the testpiece at the exhaust end. T6 measured the temperature inside the testpiece at the exhaust end.
The two wires of T2 were connected wrongly during this test so the shape of the graph for T2 is inverted in Figure 79, although the actual temperatures will not simply be the positive value of the recorded results. The values of T1 and T2 rose steadily for 10 seconds before peaking. During the explosive combustion the temperature inside the combustion chamber (T1) reached 509°C. T2 peaked during the same second.
7.8.1. Explosive Combustion

Figure 79: Thermocouple Readings During Explosive Combustion

The x-axes in both Figure 78 and Figure 79 are 128 seconds long. The initial readings of the Testo analyzer are of the ambient air present before the gas began to flow.
The Testo analyzer was unable to measure the large proportion of unburned methane during this test.

All the maxima except $O_2$ and $CO_2$ coincided at one reading (28 s) which also marked the turning point for $O_2$ (i.e. the first reading in which $O_2$ was lower than the previous reading). The peak $CO_2$ value was at 23 s, which was the moment at which all the other values began to increase. This implies that the quantity of $CO_2$ in the exhaust reached its maximum value instantly, but the other quantities (including exhaust temperature) increased for a further 5 seconds before peaking.
• The quantity of O₂ increased when the O₂ began to flow and reduced sharply following the explosion, but remained above atmospheric.

• The quantity of NO varied between 0 and 1 ppm until the explosion, then rose to 27 ppm and reduced again.

• The reported quantity of NO₂ varied between -0.2 and 0.2 ppm until the explosion then rose to 1.2 ppm and reduced again.

• The quantity of NOx (including NO and NO₂) varied between 0 and 1 ppm until the explosion, then rose to 29 ppm and reduced again.

• The reported quantity of H₂ varied between -27 and 28 ppm until the explosion, then reduced to -1340 ppm, then could not be measured (shown as 0 on the graph), then reappeared at 2350 ppm and reduced. The false negative values and inconclusive measurements resulted in a false peak on the graph a few seconds later than the other peaks. In reality the quantity of H₂ most likely peaked at the same instant as the other species.

• The reported quantity of CO₂ varied between 0.33% and 0.39% until the explosion then rose to 1.84% and reduced.

• At about a minute after the combustion the values of NO, NOx, CO and H₂ all increased slightly and O₂ reduced slightly.

• The temperature of the exhaust rose to 31.4°C during the explosion then reduced again. The ambient temperature remained between 22.2°C and 22.5°C throughout the test.

• The pressure reading did not change at all but remained at atmospheric pressure.
7.8.2. Steady State Combustion Without a Testpiece

The temperatures in the combustion chamber and at the exit of the combustion chamber can be clearly seen in Figure 81 to change with experimental parameters. When the combustion began both T1 and T2 increased rapidly for 4 seconds, remained constant for 1 second, and then increased slowly and steadily. When the flow rates were increased, T2 increased rapidly and T1 increased at an intermediate rate for 9 seconds, remained constant for 1 second, and then increased slowly. After the next increase in flow rates the temperatures took about 25 seconds to level off. When the Ar was introduced to the mix (at about 220 s) the temperatures dipped sharply and increased again. When the oxygen flow rate was increased the temperature reduced and stayed at the lower level until the methane was increased to the stoichiometric
amount, whereupon the temperature rose sharply once more. Finally the temperature rose slowly and steadily until the test ended. T3 at the end of the test is 74°C.

Figure 82: Selected Testo Analyzer Readings During Steady State Combustion Without a Testpiece

The x-axis in Figure 82 is 622 s long. The oxygen level increased sharply when the oxygen began to flow. When combustion began the level of oxygen reduced sharply and the level of CO₂ increased. As the Testo probe was exposed to ambient air mixed with exhaust gases, the level of oxygen remained close to atmospheric at all times. The level of CO₂ increased each time the combustion gas flow rates were increased.
Ar was not measured by the Testo but introduction of Ar would reduce the proportions of the other gas species. Because of the high degree of mixing of ambient air and combustion products, the introduction of Ar had no noticeable effect on any of the measurements in this test. When the oxygen was increased to the maximum level (at about 12:12:55) a noticeable increase in $O_2$ levels and decrease in $CO_2$ levels was discernible. Because of the degree of mixing it was not until the combustion gases reached their highest flow rates that oxygen levels dropped below atmospheric and quantities of incomplete combustion species became noticeable.

When the Testo probe was removed from the combustion gas stream and placed in the air exhaust tube, quantities of combustion products were lower than at the combustion exit. Over time the quantities of combustion products in the air exhaust tube increased, implying that the air exhaust had previously contained a higher proportion of ambient air than when it was blocked by the probe. This implies that ambient air was travelling into the rig from the air exhaust throughout the test. If a testpiece were present, this ambient air flow could not occur. Insertion of a testpiece, combined with a correctly sized exhaust, would drastically decrease the mixing of the combustion gases with ambient air, thereby vastly increasing the quality of the data collected.

### 7.8.3. Steady State Combustion With a Testpiece

As can be seen in Figure 83, the temperatures reacted in similar manner to the test without a testpiece. Steady state combustion was achieved, and the temperature increased. Because the testpiece exploded at the start of the test, the experiment was very similar to the previous situation, except that there was even more mixing of
combustion gases and ambient air because the rig was leaking. The data collected by the Testo analyzer in this experiment is not shown as it adds no new information.

Figure 83: Thermocouple Readings During Steady State Combustion With a Testpiece

7.8.4. Steady State Combustion Without Outer Tube Assembled

When the O₂ flow rate had reached 1.2 slpm, and the methane flow rate 0.6 slpm, the combustion was at steady state at 1000°C. At this point Ar was introduced at 0.1 slpm. There was no effect. The Ar was increased to 0.2 slpm with no effect, but when increased to 0.3, the temperature of the combustion increased. This implies that ambient air was entering the combustion chamber and cooling the gases before entry to the Testo analyzer.

The probe was then manually held in place to cover as much of the combustion chamber exit as possible. There was a noticeable increase in the combustion product
species measured by the Testo analyzer, which is visible in Figure 84 (at about 16:55:00). This implies that if the probe were to be inserted in the correct manner, the Testo readings would be vastly improved.

Figure 84: Selected Testo Analyzer Readings During Steady State Combustion

Without Outer Tube Assembled
7.8.5. Analysis of OTM Microstructure

Figure 85: Grain Size of YSZ Before Experiments

Figure 86: Grain Size of LaSrFeCr Before Experiments

It can be clearly seen in Figure 85 that the grain size of the unused YSZ is about 40 µm. Figure 86 demonstrates that the grain size of the unused LaSrFeCr is about 5 µm.
8. Conclusions

8.1. Conclusions of Literature Review

- Combustion in OTM tubes is feasible and has been achieved.

- Turbines with a working fluid composed of a mixture of CO₂ and H₂O are feasible. A turbine with an inlet temperature of 1312°C, an inlet pressure of 40 bar, and a working fluid composed of 77% CO₂ and 23% H₂O by mass has been designed. A turbine with an inlet temperature of 1400°C, an inlet pressure of 40 bar, and a working fluid composed of 62% H₂O and 38% CO₂ has been designed.

- The natural log of the oxygen partial pressure ratio across the membrane in the ZEITMOP-Separate cycle is estimated to be 1.35.

- The OFFCET cycle is not a new invention.

- The OFFCSET cycle is a new invention.

- A significant amount of research and development has been completed on OTM units suitable for use in the ZEITMOP-Separate cycle. None of the modules reviewed were suitable for use in the ZEITMOP-Combined cycle.

8.2. Conclusions Drawn from OTM Comparison

- BSCF, a perovskite, would be a stable material to use in an OTM combustor for natural gas. However, the material is not stable in a hydrogen containing environment. If the membrane were to be used as a combustor for gas containing hydrogen, e.g. for gas exiting the fuel side of a SOFC, BSCF might
not be suitable, however other perovskite materials such as LCFC would be suitable.

- Available perovskite ceramics cannot operate at a temperature above 1000°C. Fluorite membranes can operate at temperatures in excess of 1000°C, but currently have lower oxygen fluxes.
- A flux of 0.6 μmol/(cm²s) is estimated for a 1 mm thick Ce₀.₇Pr₀.₃O₂₋d fluorite membrane operating at 1300°C with an oxygen-consuming reaction on the permeate side.
- A flux of 0.72 μmol/(cm²s) is estimated for a 1 mm thick Ce₀.₇Pr₀.₃O₂₋d fluorite membrane operating at 1400°C with an oxygen-consuming reaction on the permeate side.
- The normalised flux for a 1 mm thick Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋d membrane operating at 875°C is 3.26 μmol/(cm²s) when the natural log of the oxygen partial pressure ratio across the membrane is 6.46.
- The estimated flux for a 1 mm thick Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋d membrane operating at 875°C is 0.5 μmol/(cm²s) when the natural log of the oxygen partial pressure ratio across the membrane is 1.35.
- The estimated flux for a 1 mm thick SrCo₀.₉Nb₀.₁O₃₋d membrane operating at 875°C is 0.8 μmol/(cm²s) when the natural log of the oxygen partial pressure ratio across the membrane is 1.35.
- The estimated flux for a thin-film SrCo₀.₉Nb₀.₁O₃₋d membrane operating at 875°C is 18 μmol/(cm²s) when the natural log of the oxygen partial pressure ratio across the membrane is 1.35.
- An estimate of the flux through a thin-film BSCF membrane cannot be made at this point.
• The estimated flux through a 1 mm thick perovskite unit for the ZEITMOP-Separate cycle is 0.8 \( \mu \text{mol/(cm}^2\text{s)} \), while the estimated flux through a 1 mm thick fluorite unit for the ZEITMOP-Combined cycle is 0.72 \( \mu \text{mol/(cm}^2\text{s)} \). However, both of these estimates should be taken as a guideline only. It can be concluded that the units would be of a similar order of size, and therefore design characteristics of the membrane unit other than choice of material will impact on whether the ZEITMOP-Combined has a smaller OTM module than the ZEITMOP-Separate.

• The estimated flux through a thin-film perovskite unit for the ZEITMOP-Separate cycle is 18 \( \mu \text{mol/(cm}^2\text{s)} \). No estimate can be made for a thin-film unit for the ZEITMOP-Combined cycle at this point.

• Assuming an average flux for a tubular unit based on an average temperature is an acceptable assumption.

8.3. Conclusions of Simulations

• The OTM unit will operate as an almost perfect heat exchanger.

• The transfer of heat from the air stream to the CO\textsubscript{2} stream in the ZEITMOP-Combined plant increases efficiency at high combustion temperatures and low combustion pressures.

• At a combustion temperature of 1300°C and a combustion pressure of 30 bar the flow entering the combustion products turbine in the ZEITMOP-Combined with heat transfer contains 81% CO\textsubscript{2} and 19% H\textsubscript{2}O by mass. At 1300°C and 5 bar it contains 86% CO\textsubscript{2} and 14% H\textsubscript{2}O, and at 1500°C and 5 bar it contains 83% CO\textsubscript{2} and 14% H\textsubscript{2}O by mass.
• The optimal conditions for the ZEITMOP-Combined cycle are: combustion temperature as high as possible for the turbine used, combustion pressure 3-5 bar, CO₂ delivery pressure as low as possible for end application.

• At an oxygen flux of 18 μmol/(cm² s) the OTM unit will be of a similar size to the heat exchanger units.

• The OFFCET cycle has an efficiency that compares well with the ZEITMOP cycle, and merits further investigation.

• A mechanical design has been developed for the first time for the ZEMPES, and has been presented here. The design has been simplified using standard vehicle turbocompressors resulting in a reduction in efficiency of 11 percentage points. The system is an appropriate size to power a bus and has been presented placed on a bus chassis.

8.4. Conclusions of Experimental Work

• The rig is capable of delivering a hot stream of combustion products to the testpiece.

• The rig has the potential to provide useful data if the Testo Analyzer probe is used in the correct manner.

• The grain size of the YSZ samples purchased is about 40 μm diameter.

• The grain size of the LsSrFeCr is about 5 μm diameter.
8.5. Main Conclusions of This Thesis

The efficiency of ZEITMOP-Combined with a perovskite unit would be very low due to the low operating temperature. The efficiency of ZEITMOP-Combined with a fluorite unit may be higher than the efficiency of ZEITMOP-Separate at the same combustion temperature. A fluorite OTM combustion unit operating at 1400°C would be of a similar size to a perovskite OTM air separation unit operating at 875°C. The OTM unit is likely to be of a similar size to the heat exchangers in the cycle.

The efficiency of ZEITMOP-Combined is increased by heat transfer from the combustion and air streams to the CO₂ stream. The effect of heat transfer on the ZEITMOP-Separate cycle must be investigated in more detail. It seems likely that the optimized ZEITMOP-Combined and ZEITMOP-Separate cycles will have efficiencies in a similar range.
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Appendix A: Equation of State of Span and Wagner

The Equation of State of Span and Wagner is a method of calculating the dimensionless Helmholtz energy. From this value other quantities are calculated. The equation developed, the method used to find the various constants and coefficients, and the level of agreement with experimental data is described by Span and Wagner.\textsuperscript{78}

\[ \phi(\delta, \tau) = \phi^0(\delta, \tau) + \phi^\Gamma(\delta, \tau) \]

\( \phi \)  Dimensionless Helmholtz Energy

\[ \phi = A / RT \]

A = Helmholtz Energy \hspace{1cm} A = h – RT – Ts \hspace{1cm} [kJ/kg]

R = Specific Gas Constant \hspace{1cm} For CO\textsubscript{2}: R= 0.188924 \hspace{1cm} [kJ/kgK]

T = Temperature \hspace{1cm} [K]

s = Specific entropy \hspace{1cm} [kJ/kgK]

\( \phi^0 \)  Ideal Dimensionless Helmholtz Energy

\( \phi^\Gamma \)  Residual Dimensionless Helmholtz Energy

\( \delta \)  Reduced density \hspace{1cm} \delta = \rho/\rho_c

\( \rho \)  density \hspace{1cm} [kg/m\textsuperscript{3}]

\( \rho_c \)  critical density \hspace{1cm} For CO\textsubscript{2}: \rho_c = 467.6 \hspace{1cm} [kg/m\textsuperscript{3}]

\( \tau \)  Inverse reduced temperature \hspace{1cm} \tau = T_c/T

T\textsubscript{c}  = critical temperature \hspace{1cm} For CO\textsubscript{2}: T\textsubscript{c} = 304.1282 \hspace{1cm} [K]

For carbon dioxide, \( \phi^0 \) can be found from:

\[ \phi^0(\delta, \tau) = \ln(\delta) + a^0_1 \delta + a^0_2 \delta \ln(\tau) + \sum_{i=4}^{8} a^0_i \ln\left[1 - \exp\left(-\tau \theta^0_i\right)\right] \]
where:

<table>
<thead>
<tr>
<th>i</th>
<th>$\theta_i^0$</th>
<th>$\alpha_i^0$</th>
<th>i</th>
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<td>0.621 052 48</td>
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<td>6.777 08</td>
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<td>3.151 63</td>
<td>8</td>
<td>0.083 276 78</td>
<td>27.087 92</td>
</tr>
</tbody>
</table>

$\phi^i$ can be found from:

$$
\phi^i(\delta, \tau) = \sum_{i=1}^{31} n_i \delta_i^d \tau_i^d + \sum_{i=35}^{40} n_i \delta_i^d \tau_i^d e^{-\delta_i} + \sum_{i=35}^{40} n_i \delta_i^d \tau_i^d e^{-\alpha_i (\delta - \delta_i)^2 - \beta_i (\tau - \tau_i)^2} + \sum_{i=40}^{42} n_i \Delta^j \delta e^{-C_i (\delta - \delta_i)^2 - D_i (\tau - \tau_i)^2}
$$

where:

$$
\Delta = \left\{ (1 - \tau) + A_i (\delta - 1)^2 \right\}^{\frac{1}{2}} + B_i (\delta - 1)^3
$$

and where:

<table>
<thead>
<tr>
<th>i</th>
<th>$n_i$</th>
<th>$d_i$</th>
<th>$t_i$</th>
</tr>
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<tbody>
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<td>1</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.293 854 759 427 40 $\times 10^1$</td>
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<td>0.75</td>
</tr>
<tr>
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<td>−0.558 671 885 349 34 $\times 10^1$</td>
<td>1</td>
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<td>5</td>
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<td>2</td>
<td>0.75</td>
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<tr>
<td>6</td>
<td>0.548 033 158 977 67 $\times 10^6$</td>
<td>2</td>
<td>2.00</td>
</tr>
<tr>
<td>7</td>
<td>0.122 794 112 203 35 $\times 10^6$</td>
<td>3</td>
<td>0.75</td>
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</table>
Other properties can be found from the Helmholtz function as shown below:

\[
\begin{array}{ccccccc}
  i & n_i & d_i & t_i & c_i & \frac{1}{n_i} & \frac{1}{d_i} \\
  8 & 0.216 & 0.054 & 1.50 & 10 & 1.00 & 1.50 \\
  9 & 0.158 & 0.054 & 1.50 & 10 & 1.00 & 1.50 \\
 10 & -0.231 & 0.054 & 2.50 & 10 & 1.00 & 2.50 \\
 11 & 0.584 & 0.014 & 3.60 & 10 & 1.00 & 3.60 \\
 12 & -0.555 & 0.053 & 1.50 & 10 & 1.00 & 1.50 \\
 13 & 0.489 & 0.094 & 2.20 & 10 & 1.00 & 2.20 \\
 14 & -0.262 & 0.085 & 0.01 & 10 & 1.00 & 0.01 \\
 15 & 0.624 & 0.016 & 1.70 & 10 & 1.00 & 1.70 \\
 16 & -0.121 & 0.025 & 2.00 & 10 & 1.00 & 2.00 \\
 17 & -0.370 & 0.085 & 2.00 & 10 & 1.00 & 2.00 \\
 18 & -0.167 & 0.004 & 2.60 & 10 & 1.00 & 2.60 \\
 19 & -0.119 & 0.036 & 3.70 & 10 & 1.00 & 3.70 \\
 20 & 0.456 & 0.062 & 7.60 & 10 & 1.00 & 7.60 \\
 21 & 0.156 & 0.028 & 8.00 & 10 & 1.00 & 8.00 \\
 22 & -0.744 & 0.073 & 5.50 & 10 & 1.00 & 5.50 \\
 23 & -0.173 & 0.049 & 3.00 & 10 & 1.00 & 3.00 \\
 24 & -0.218 & 0.021 & 2.50 & 10 & 1.00 & 2.50 \\
 25 & 0.243 & 0.065 & 5.90 & 10 & 1.00 & 5.90 \\
 26 & -0.374 & 0.034 & 3.60 & 10 & 1.00 & 3.60 \\
 27 & 0.143 & 0.057 & 16.0 & 10 & 1.00 & 16.0 \\
 28 & -0.134 & 0.069 & 3.20 & 10 & 1.00 & 3.20 \\
 29 & -0.231 & 0.025 & 16.0 & 10 & 1.00 & 16.0 \\
 30 & 0.123 & 0.025 & 3.20 & 10 & 1.00 & 3.20 \\
 31 & 0.210 & 0.040 & 10.0 & 10 & 1.00 & 10.0 \\
 32 & -0.339 & 0.015 & 2.60 & 10 & 1.00 & 2.60 \\
 33 & 0.559 & 0.047 & 28.0 & 10 & 1.00 & 28.0 \\
 34 & -0.303 & 0.051 & 18.0 & 10 & 1.00 & 18.0 \\
 35 & -0.213 & 0.064 & 8.80 & 10 & 1.00 & 8.80 \\
 36 & 0.266 & 0.041 & 4.90 & 10 & 1.00 & 4.90 \\
 37 & -0.240 & 0.027 & 12.0 & 10 & 1.00 & 12.0 \\
 38 & -0.283 & 0.034 & 23.0 & 10 & 1.00 & 23.0 \\
 39 & 0.212 & 0.044 & 24.0 & 10 & 1.00 & 24.0 \\
 40 & -0.666 & 0.042 & 7.60 & 10 & 1.00 & 7.60 \\
 41 & 0.729 & 0.086 & 2.40 & 10 & 1.00 & 2.40 \\
 42 & 0.550 & 0.086 & 1.20 & 10 & 1.00 & 1.20 \\
\end{array}
\]

Other properties can be found from the Helmholtz function as shown below:
<table>
<thead>
<tr>
<th>Property and common thermodynamic definition</th>
<th>Relation to the reduced Helmholtz energy ( \psi ) and its derivatives(^*)</th>
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<tbody>
<tr>
<td>( p(T, p) = -\left( \frac{\partial \psi}{\partial T} \right)_T )</td>
<td>( p(\delta, \tau) = 1 + \delta \phi )</td>
</tr>
<tr>
<td>( s(T, p) = -\left( \frac{\partial \psi}{\partial S} \right)_T )</td>
<td>( \frac{p}{RT} = 1 + \delta \phi )</td>
</tr>
<tr>
<td>( u(T, p) = -T\left( \frac{\partial \psi}{\partial T} \right)_p )</td>
<td>( \tau(\delta, \tau) = \tau(\delta \phi + \phi) - \delta \tau - \phi )</td>
</tr>
<tr>
<td>Isochoric heat capacity: ( c_v(T, p) = \left( \frac{\partial u}{\partial T} \right)_p )</td>
<td>( \frac{v(\delta, \tau)}{RT} = \tau(\delta \phi + \phi) )</td>
</tr>
<tr>
<td>Enthalpy: ( h(T, p) = T\left( \frac{\partial u}{\partial T} \right)_p )</td>
<td>( c_v(\delta, \tau) = -\frac{1}{R}(\phi_\tau^* + \phi_\tau^*) )</td>
</tr>
<tr>
<td>Isobaric heat capacity: ( c_p(T, p) = \left( \frac{\partial h}{\partial T} \right)_p )</td>
<td>( \frac{h(\delta, \tau)}{RT} = 1 + \tau(\delta \phi + \phi) + \delta \phi )</td>
</tr>
<tr>
<td>Saturated liquid heat capacity: ( c_f(T) = \left( \frac{\partial h}{\partial T} \right)_p + \left( \frac{\partial h}{\partial T} \right)_v )</td>
<td>( c_p(\delta, \tau) = -\frac{1}{R}(\phi_\tau^* + \phi_\tau^*) + \left( \frac{1 + \delta \phi}{1 + \delta \phi} \right)^2 )</td>
</tr>
<tr>
<td>( (\delta p_v / \delta T)<em>T \left( \frac{\partial h}{\partial h} \right)</em>{T} )</td>
<td>( c_v(\delta, \tau) = -\frac{1}{R}(\phi_\tau^* + \phi_\tau^*) + \frac{1 + \delta \phi}{1 + \delta \phi} )</td>
</tr>
<tr>
<td>Speed of sound: ( u(T, p) = \left( \frac{\partial p}{\partial \rho} \right)_T )</td>
<td>( \frac{w(\delta, \tau)}{RT} = \frac{1 + \delta \phi}{1 + \delta \phi} + \frac{(1 + \delta \phi) - \delta \phi \phi}{1 + \delta \phi} )</td>
</tr>
<tr>
<td>Joule-Thomson coefficient: ( \mu(T, p) = \left( \frac{\partial u}{\partial T} \right)_p )</td>
<td>( \mu(\delta, \tau) = \delta \phi \phi + \delta \phi \phi + \delta \phi \phi )</td>
</tr>
<tr>
<td>Fugacity: ( \ln(p(T, p)) = \int_{\rho_0}^{p(T, p)} \frac{\ln(p(T, p) - p) \rho_{T, p}}{p_{T, p}} dp )</td>
<td>( \ln(\Phi(\delta, \tau)) = \phi^* - \delta \phi^* - \ln(1 + \delta \phi) )</td>
</tr>
<tr>
<td>Second virial coefficient: ( B(T) = \lim_{\rho \to 0} \left( \left( \frac{\partial u}{\partial \rho} \right)<em>T \right)</em>{\rho = 0} )</td>
<td>( B(\tau) \rho_T = \lim_{\rho \to 0} \phi^* )</td>
</tr>
<tr>
<td>Third virial coefficient: ( C(T) = \lim_{\rho \to 0} \left( \left( \frac{\partial u}{\partial \rho} \right)<em>T \right)</em>{\rho = 0} )</td>
<td>( C(\tau) \rho_T^2 = \lim_{\rho \to 0} \phi^* )</td>
</tr>
</tbody>
</table>

\(^*\) \( \phi_\tau = \frac{\partial \phi}{\partial \tau} \), \( \phi_\delta = \frac{\partial \phi}{\partial \delta} \), \( \phi_{\delta \tau} = \frac{\partial \phi}{\partial \delta \partial \tau} \), \( \phi_{\delta \tau} = \frac{\partial \phi}{\partial \delta \partial \tau} \), and \( \phi_{\delta \delta} = \frac{\partial \phi}{\partial \delta \partial \delta} \).
Publications

Posters
1. Poster in Embark Symposium 2004
2. Poster in Embark Symposium 2005
3. Poster in Bernard Crossland Symposium 2006

Papers presented at conferences


**Journal papers**
