

Politecnico di Torino

Master's Degree in MECHANICAL ENGINEERING



**Politecnico
di Torino**

Master's Degree Thesis

**Experimental characterization and process
simulation of thermochemical redox cycles
with LSMA perovskite**

Supervisors:

Prof. Massimo Santarelli

Dr. Domenico Ferrero

Dr. Francesco Orsini

Candidate:

Giuseppe Rechichi

December 2022

Abstract

Rapid economic growth has contributed to the increasing energy demand observed nowadays with a consequent increase in the use of fossil fuels. Their combustion and following carbon dioxide (CO_2) emissions recently arose as a cause of concern due to the adverse effect on the environment, since CO_2 has been widely recognized as a major greenhouse gas and as the main cause of global warming. Energy demand is still expected to grow in the decades to come, thus, new pathways for its production should be pursued. Renewable energy sources (RES) have been identified as the long term solution to reduce CO_2 emissions, but their intermittency can hinder the effectiveness of such technologies. Energy storage is therefore a crucial remedy to this issue, and, specifically chemical energy storage, when coupled with solar energy plants, has an undoubted potential. Solar energy can be converted and stored into chemicals such as hydrogen and/or carbon monoxide (H_2 and/or CO) through dissociation of zero-energy molecules such as H_2O and or CO_2 , respectively. The synthetic molecules produced in this way are referred to as solar fuels. A mixture of the two - *i.e.* syngas - can serve as a precursor for more complex fuel synthesis. If a carbon capture (CC) technology is coupled with solar fuels production plants, the captured CO_2 can be used as raw material to the process, thereby closing the carbon cycle ideally with zero emissions.

Among the different pathways to produce solar fuels, solar thermochemical redox cycles are a promising option. Such cycles are composed of two reaction steps. The first step is described by the higher temperature endothermic reduction, in which the oxygen carrier (OC) is reduced upon heating with concentrated solar thermal (CST) energy. The second step is the lower temperature oxidation, in which the reduced OC is re-oxidized with H_2O to produce H_2 , or with CO_2 to produce CO . In this work, $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_3$ (LSMA) perovskite was investigated as OC in CO_2 based oxidation cycles. This material has been studied extensively in literature due to its excellent redox performances when compared with perovskites tested for the

same application. Experimental tests were carried out in the CO_2 Circle Lab at Environment Park (Turin). Two different experimental techniques were used to study the CO production starting from CO_2 , one involving a tubular microreactor coupled with online evolved gas analysis (EGA) connected in series, and the other involving a thermogravimetric analyzer (TGA). The tests allowed to assess the material behavior in the examined conditions and the CO production yield. The information on the yield was the used within a simplified reactor model developed with Aspen Plus® software. The aim of the numerical model was to give a first estimate of the process efficiency, although several simplifying assumptions were made, and to show the potential of combining experimental tests with process simulation. Some hypotheses were needed in the material modelling, since the investigated perovskite was not available in the software database. More work will be carried out in the future in order to define the actual material properties and enhance the coupling between experiments and simulation.

*To whom, in each and every
way, helped me out along this
journey...*

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Chapter 1

Introduction

1.1 Greenhouse Gases and climate change

Emissions of Greenhouse Gases (GHG) have been growing for the past decades (Figure 1.1) and are widely recognized as the principal cause of global warming and climate change. According to the Climate Change Synthesis Report of 2014 [5] by the Intergovernmental Panel for Climate Change (IPCC), the effect of anthropogenic greenhouse gas emissions are extremely likely to constitute the dominant factor in causing the observed warming since the mid-20th century. The energy sector is the main responsible of CO_2 emissions and the energy demand is expected to grow in the decades to come. Global CO_2 emissions from energy combustion and industrial processes grew to 36.3 Gt in 2021, setting a record high [1]. Therefore, in order to reduce the effects of climate change it is important to act on the energy sector. If CO_2 emissions keep increasing at the current pace, it will not be possible to fulfill the commitment of the Paris Agreement of 2015, a legally binding international treaty on climate change. It was adopted by 196 countries at COP21 in Paris, its goal is to limit global warming to well below 2, preferably 1.5°C , compared to pre-industrial levels. The energy-related CO_2 emissions are caused by the combustion of fossil fuels, mainly coal, oil and natural gas. Coal consumption emitted 15.3 Gt of CO_2 in 2021, oil 10.7 Gt and natural gas 7.5 Gt [1]. Fossil fuels constitute the majority of the primary energy sources used at global level, making up 84% of the global primary energy in 2021 [2]. The remaining consumption derives from nuclear energy and renewables. Figure 1.2 shows the world primary energy consumption divided by source from 2000 to 2021. The total energy consumption increased every year

except 2009 and 2020, where it decreased due to the economic crisis and the COVID pandemic, respectively. Among the main drivers of energy use there are, in fact, population size and economic activity [5]. As the world population is expected to grow in the coming years, the world energy consumption is expected to increase as well. An important challenge in the years to come will be meeting an increasing energy demand without increasing the GHG emissions at the same time.

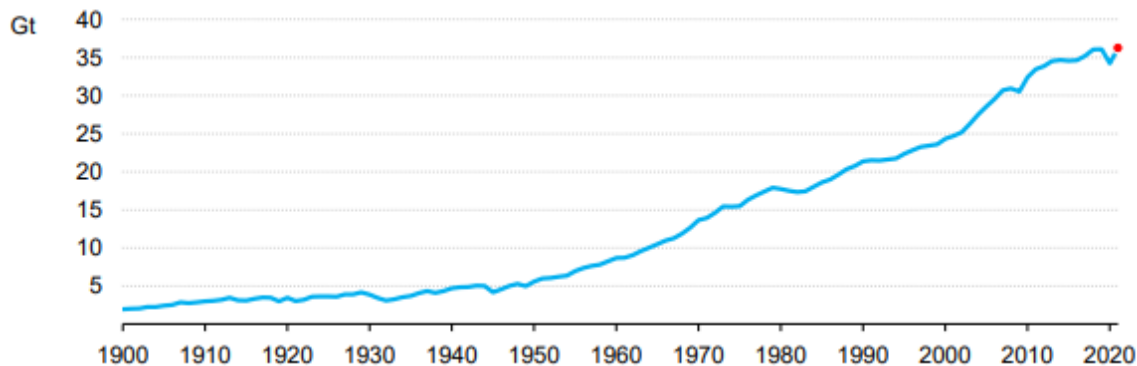


Figure 1.1: Total CO_2 emissions from energy combustion and industrial processes, 1900-2021 [1].

1.2 Renewables energies and solar fuels

A first step in reducing carbon emissions is to use energy that does not come from fossil fuel resources. The share of renewable energies (excluding hydroelectric energy) in global power generation reached almost 13% in 2021 [2], continuing a rising trend driven by a strong expansion in solar and wind energy. Solar and wind constitute the main sources through which renewable energy is produced, other types of renewable energy sources are hydroelectric, geothermal and biomass. A crucial issue regarding the substitution of fossil fuels with solar and wind energy is the intermittency of the source. While fuels can be easily stored and used when needed, the availability of sun and wind changes during the day and from one day to another. Therefore, methods to store renewable energy when available are needed. Globally, the excess of available renewable energy can be much higher than the global demand. It has been estimated that the solar radiation reaching the Earth surface in one year is approximately 6000 times greater than the global energy consumption [6]. A possible method to tackle this issue is to convert renewable energy into storable fuels. By doing so, fossil fuels can be replaced in their applications. As solar energy is employed in the production

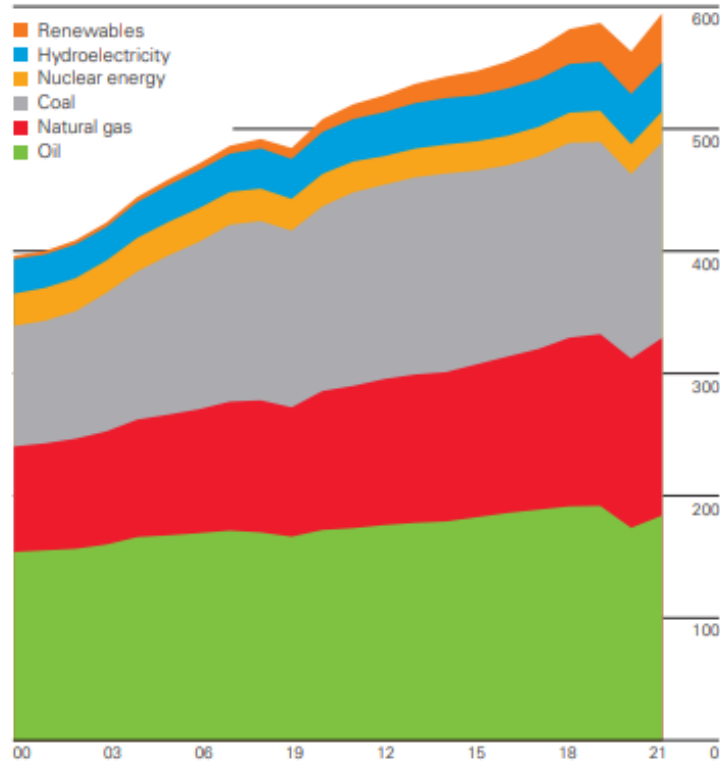


Figure 1.2: Global primary energy consumption from 2000 to 2021 divided by source [2].

of such fuels, they are generally referred to as "solar fuels". Solar fuels can be carbon-free, like solar hydrogen, and do not produce CO_2 during combustion, or can cause CO_2 emissions as they contain carbon atoms. However, if Carbon Capture and Utilization (CCU) systems are employed, the solar fuels containing carbon would only produce CO_2 that was previously captured from the atmosphere.

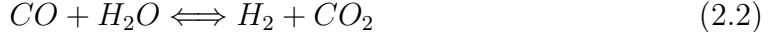
Chapter 2

Literature Review

2.1 Carbon Capture and Sequestration (CCS)

The current state of greenhouse gas emissions suggests that achieving net-zero CO_2 emissions by mitigation must be accompanied by further CO_2 removal on a timetable for decarbonization within the coming two to three decades to limit climate extremes [7]. Carbon capture and sequestration is a physical process which involves in the capturing of CO_2 and its storage. CO_2 can be separated from other compounds at different stages of the combustion. In particular, there are three CO_2 capturing systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion [8]. With the post-combustion process, CO_2 is removed from the flue gas after combustion has taken place. Post-combustion technologies are the preferred option for retrofitting existing power plants. However, the major challenge for post-combustion CO_2 capture is its large parasitic load. Since the CO_2 level in combustion flue gases is normally quite low (12 – 14% for coal-fired power plants and 3 – 4% for natural gas turbines [9]), the energy penalty and associated costs for the capture unit to reach the concentration of CO_2 needed for transport and storage are elevated. In the pre-combustion process, the fuel (normally coal or natural gas) is pre-treated before combustion. For coal, the pre-treatment involves a gasification process which forms syngas, a mixture of CO and H_2 (Eq. 2.1). The syngas will then undergo water gas shift reaction with steam forming more H_2 while the CO gas will be converted to CO_2 (Eq. 2.2):





The high CO_2 concentration in the H_2/CO_2 fuel gas mixture facilitates the CO_2 separation. Natural gas, as it mainly contains CH_4 , can be reformed to syngas containing H_2 and CO (Eq. 2.3).



In oxyfuel combustion, oxygen, instead of air, is used for combustion. This reduces the amount of nitrogen present in exhaust gas that affects the subsequent separation process. Substantial reduction in thermal NO_x is another advantage of this process. With the use of pure oxygen for the combustion, the major composition of the flue gases is CO_2 , water, particulates and SO_2 . Particulates and SO_2 can be removed and the remaining gases contain high concentration of CO_2 . They can therefore be compressed, transported and stored. This process is technically feasible but consumes large amount of oxygen coming from an energy intensive air separation. Pre-combustion is mainly applied to coal-gasification plants, while post-combustion and oxyfuel combustion can be applied to both coal and gas fired plants. Post-combustion is currently the most mature process for CO_2 capture. On the cost side, Gibbins and Chalmers [8] compared the three technologies for both gas and coal-fired plants. They reported that for coal-fired plants the pre-combustion technology presented the lowest cost per tonne of CO_2 avoided, while the post-combustion and oxyfuel technologies are of similar costs. However, for gas-fired plants, the cost per tonne of CO_2 avoided for the post combustion capture was almost 50% lower than the other two capture technologies. Moreover, the post-combustion CO_2 capture is normally the least efficient option, with an energy penalty of about 8% and 6% for the coal-fired and gas-fired plants, respectively [8]. The most common CO_2 separation processes are chemical and physical absorption in which CO_2 is removed via liquid solvent. In physical absorption, CO_2 is physically captured on the surface of the solvent with high absorption capacities at high pressures. In the chemical process, instead, the separation takes place with alkaline solvents such as monoethanolamine (MEA). Then, there is a process of regeneration of the CO_2 -rich solvent by heating. Once CO_2 is separated from the rest of the flue gas components, it needs to be transported to the storage site or to the facilities for industrial utilization. Depending on the volumes involved, a variety of means of transport may be utilized, ranging from road tankers to ship and pipelines. It is possible to use ship tankers, with technologies derived from LPG carriers, to transport CO_2 offshore [8]. Pipelines,

instead, are considered to be the most viable method for onshore transport of high volume of CO_2 through long distances. They are also the most efficient way for CO_2 transport when the source of CO_2 is power plant which lifetime is longer than 23 years. For shorter period road and rail tankers are more competitive [8]. In order to optimize the mass/volume ratio CO_2 is carried as dense phase wither in liquid or supercritical conditions. Supercritical is the preferred state for CO_2 transported by pipelines, which implies that the pipelines operative temperature and pressure should be maintained within the CO_2 supercritical envelop, i.e. $32.1^\circ C$ and $72.9 atm$. The typical range of pressure and temperature for a CO_2 pipeline is between 85 and 150 bar, and between $13^\circ C$ and $44^\circ C$ to ensure a stable single-phase flow through the pipeline. The drop in pressure due tu the reduction of the hydraulic head along the pipeline is compensated by adding re-compression stations. Larger diameter pipelines allow lower flow rates with smaller pressure drop and therefore a reduced number of re-compression stations. On the other hand, larger pipelines are more expensive therefore a balancing of costs need to be considered. CO_2 can be stored into geological formations such as deep saline aquifers which have no other practical use and oil or gas reservoirs. Geological storage is at present considered to be the most viable option for the storage of large CO_2 quantities. A typical geological storage site can hold several tens of millions tonnes of CO_2 trapped by different physical and chemical mechanism. Suitable geological sites for CO_2 storage have to be carefully selected. General requirements for geological storage of CO_2 include appropriate porosity, thickness, and permeability of the reservoir rock [8]. Requirements such as distance from the source of CO_2 , effective storage capacity, pathways for potential leakage and in general economic constrains may limit the feasibility of being a storage site. Three different geological formations are commonly considered for CO_2 storage: depleted oil and gas reservoir, unmineable coal beds, and saline aquifers. Deep ocean storage is also a feasible option for CO_2 storage although environmental concerns (such as ocean acidification and euthophication) will likely limit its application. After capture, the high CO_2 content stream can be transported for geological storage or for CO_2 utilization, in which case the technology is referred as to Carbon Capture and Utilization (CCU). CO_2 can be reused in industry, agriculture, food beverage, refrigerants, fire extinguisher gases and energy production. CCU seeks not only to reduce the volume of emissions to the atmosphere but also to obtain a benefit through the use of CO_2 in different types of industrial processes, replacing conventional raw materials. Current CO_2 utilization account for only 2% of emissions, but forecasts predict chemical utilization could mitigate 700 megatons of CO_2 per year [8]. In recent years, solar thermochemical cycles have captured the scientific community's attention. This technology consists in splitting CO_2 through

thermochemical redox cycles as an efficient pathway to directly convert concentrated solar energy into storable and dispatchable chemical form.

2.2 Solar thermochemical fuel production

Solar energy is a ubiquitous and essentially unlimited resource, it offers the ability to generate electricity via solar photovoltaic (PV), provide hot water for domestic heating application, of any number of other thermally demanding applications. The major caveats with all of these methods are related to the sun’s intermittency and, therefore, they should be integrated with storage technologies if they are to be used on demand [10]. The conversion of incident sunlight directly to chemical fuel such as molecular hydrogen or fuel precursors like synthesis gas (syngas) offers the potential to efficiently store solar energy, transport it and utilize on demand. Given that the current transportation infrastructure is largely based on the use of liquid hydrocarbon fuels, efficient conversion of concentrated solar energy into fungible fuels provides a pathway to begin the transition away from fossil fuels and towards renewable fuel sources. There are a variety of methods to convert sunlight to fuels through dissociation of H_2O and/or CO_2 , and most of them are low temperature photon-driven approaches that take advantage of a portion of the sun’s solar spectrum that has sufficient energy to drive the process of interest, the remainder of the spectrum is not able of being utilized. Thermochemical approaches, instead, utilize concentrated sunlight as a thermal input to drive the dissociation of H_2O and CO_2 . In such an approach, the entire solar spectrum is absorbed thermally and, therefore, provides a thermodynamically attractive pathway to solar fuel production [11]. A variety of mature point-focusing concentrating technologies such as parabolic dishes or heliostat fields may be utilized to focus the sun’s radiant energy enough to drive number of solar thermochemical processes (STC) at elevated temperatures, usually in the range of 873-2273K [12]. There are several approaches to convert absorbed solar energy to fuels via thermally driven pathways. The primary pathways through which solar thermochemical conversion to H_2 or synthesis gas can be achieved are either fuel reforming processes (e.g. steam methane reforming) where a fuel and H_2O (and sometimes CO_2) are used as feedstocks, or thermolysis/redox cycles in which no fuel precursor is required and only H_2O or CO_2 are used as feedstoks (Figure 2.1) [13].

2.2.1 Solar Reforming Processes

For most fuel reforming processes that are non-solar, some of the carbonaceous feedstock is combusted to provide the heat necessary heat to drive an endothermic re-

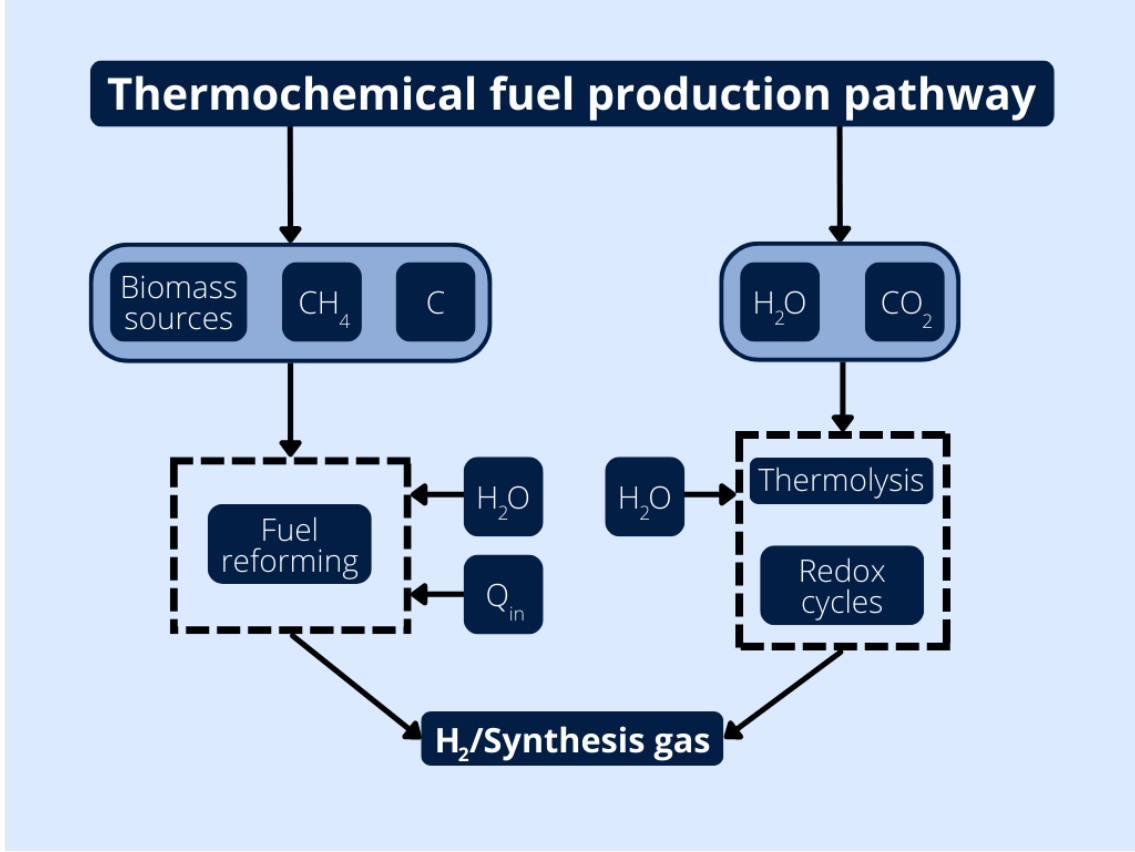
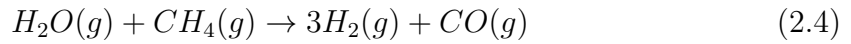
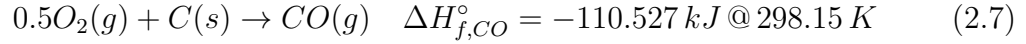
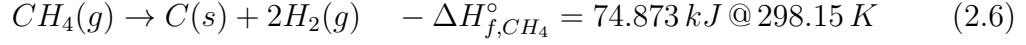
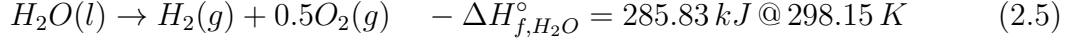


Figure 2.1: Thermochemical fuel production pathways that utilize concentrated sunlight to drive an endothermic reaction resulting in H_2 or synthesis gas. On the left are fuel reforming cycles driving an endothermic reforming reaction and on the right are pathways that only utilize H_2O or CO_2 as net feedstocks.

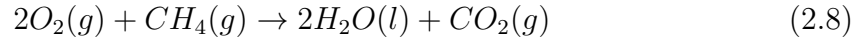
forming reaction (e.g. $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$). As a result, the net heating value of the products is less than the primary feedstock. For example, consider steam methane reforming which is the most established method to produce industrial H_2 . Here, the net steam reforming reaction may be expressed by:



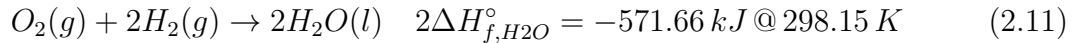
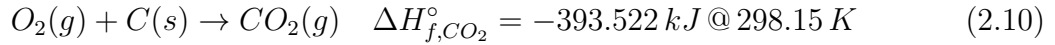
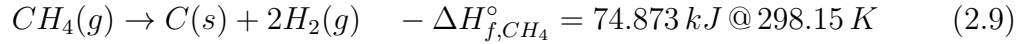
Equation 2.4 is the net reaction of the following three formation reactions:



where $\Delta H_{f,i}^\circ$ is the standard formation enthalpy of species i at standard conditions (298.15 K). Thus, the net reaction enthalpy of the steam reforming reaction ($-\Delta H_{f,H_2O}^\circ - \Delta H_{f,CH_4}^\circ + \Delta H_{f,CO}^\circ$) is 250.2 kJ at 298.15 K. To drive this endothermic reaction, some of the methane feedstock is combusted according to the following reaction:



which is the product of the following formation reactions.

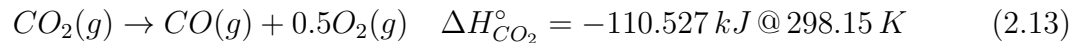
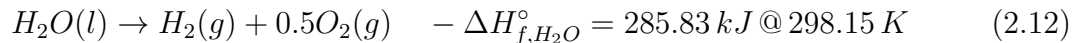


Thus, the net reaction enthalpy ($-\Delta H_{f,CH_4}^\circ + \Delta H_{f,CO_2}^\circ + 2\Delta H_{f,H_2O}^\circ$) is -890.3 kJ at 298.15 K. Therefore, for every mole of CH_4 that is reformed (Eqn. 2.4), 250.2 kJ are required, 0.28 moles must be combusted (Eqn. 2.8) to provide the required process heat, at a minimum. In reality, it is substantially greater because of inefficiencies and because the reaction enthalpy decreases at higher temperatures. In solar driven fuel reforming processes, solar energy is used as process heat to drive the endothermic reforming reaction rather than combustion of the feedstock [14]. As a result, the feedstock is upgraded because the heating value of the products are greater than the primary feedstock, and solar energy is effectively stored in chemical form. A wide variety of solar reforming processes have been proposed in the literature, and compared to the non fuel reforming processes on the right side of Figure 2.1, these

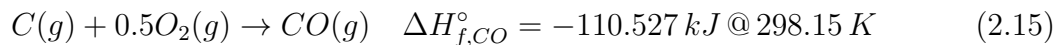
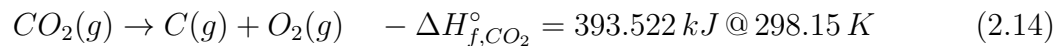
typically occur at relatively moderate temperatures (e.g. $< 1000^\circ\text{C}$). Therefore, they are practically more straightforward because demands on reactor and construction materials are not as strict. As a result, these technologies are relatively mature and several concepts have been tested at the prototype reactor scale. It is important to note that solar reforming processes are not carbon neutral unless the carbon comes from a source that is continuously replenished by CO_2 from the atmosphere.

2.2.2 Solar Driven Thermolysis

Conceptually, the simplest path to H_2 or CO is the direct thermolysis of H_2O or CO_2 . Additionally, these pathways are inherently carbon neutral, as opposed to fuel reforming processes, because their net inputs are simply the by-products of fuel combustion. Their net chemical reactions are shown below [13].



Where $\Delta H_{\text{CO}_2}^\circ$ is the enthalpy change of CO_2 thermolysis referenced to standard state. This reaction enthalpy change is determined by recognizing that it is the sum of the following two formation reactions ($\Delta H_{\text{CO}_2}^\circ = -\Delta H_{f,\text{CO}_2}^\circ + \Delta H_{f,\text{CO}}^\circ$) shown below.

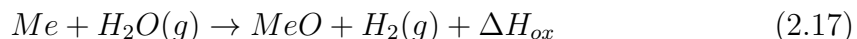
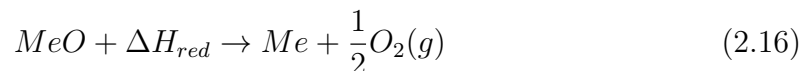


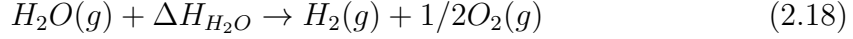
While conceptually simple, these reactions are difficult to achieve in practice because of their extreme temperatures (usually $> 2273 \text{ K}$) and the favorability of the reverse reactions as the gaseous products cool. Thus, to prevent product recombination, thermolysis reactions are usually conducted in a high temperature oxygen conducting ceramic where the outside of the ceramic is kept at allow oxygen partial pressure. As the reaction progresses, the produced O_2 diffuses across the solid membrane and away from either H_2/CO , thereby preventing recombination. Usually thermolysis reaction temperatures are limited by the temperature stability of the oxygen conducting ceramic (usually less than 2273 K or other reactor construction materials

and are therefore conducted well below where they are thermodynamically favorable at ambient pressure. As a result, reaction extents are usually very small or a large amount of mechanical work (e.g. vacuum pumping) is required. In both instances, the efficiency is hindered. In the former, an excess of thermal energy is supplied that may only be recovered through efficient, high temperature heat exchange, in the latter, there are significant second law losses associated with producing the work. Further, even if materials were stable enough to operate where the reactions are more thermodynamically favorable, the re-radiation losses would be so large that produce a severe and negative effect on the efficiency.

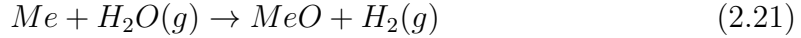
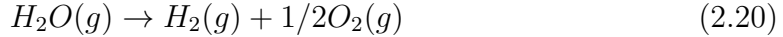
2.2.3 Thermochemical Redox-Cycles

It is possible to decrease the operating temperature of H_2O or CO_2 thermolysis while still utilizing only thermal energy through the implementation of a redox cycle where the thermolysis reaction is split into two or more reactions. One of them has a larger entropy change than the net entropy change of the reaction. In general, as the number of reactions increases, the upper temperature decreases but the complexity associated with the process increases. Therefore, for practical reasons, the bulk of interest in H_2O/CO_2 redox splitting cycles in recent years has been focused on two-step cycles. Compared to the direct thermal dissociation of H_2O or CO_2 , the two-step metal-oxide based thermochemical redox cycles allow for significantly reduced operating temperatures and eliminate the risk of explosive recombination of products by producing oxygen and the desired fuel in separate steps. They drive a high temperature endothermic reduction of a solid metal oxide (MeO) in the first step, temperatures are usually greater than $1000^\circ C$ and dependent on the metal oxide used. Following reduction, the reduced metal oxide is then subsequently oxidized in an exothermic reaction at lower temperatures by H_2O or CO_2 and producing gaseous H_2 or CO . The H_2 or CO produced may be used directly to generate power through combustion or electrochemical oxidation. Additionally, the mixture of the two, syngas, may be further processed to fungible liquid hydrocarbon fuels such as kerosene, diesel, and gasoline via catalytic processes such as Fischer-Tropsch (FT) synthesis [15]. The two step MeO based redox cycle for H_2O splitting and the net reaction is shown below.





The reason why these cycles result in a lower operating temperature than the direct thermolysis of H_2O (or CO_2) is that the first step takes advantage of fact that the entropy change (ΔS) required to reduce the oxide is greater than for water dissociation (but also enthalpy is greater). Figure 2.2a shows the Gibbs free energy change (ΔG) for the reduction reaction of a hypothetical metal oxide alongside the H_2O thermolysis reaction. The equilibrium for both reaction is dictated by ΔG , where less than 0 indicates the reaction is more favorable in forward direction and greater than zero more favorable in reverse direction. $\Delta G = \Delta H - T\Delta S$, as seen in Figure 2.2a the entropy change is greater (steeper slope) for the oxide reduction, resulting in $\Delta G = 0$ at a lower temperature, meaning the reaction is more likely to proceed in the forward direction compared to thermolysis. The oxidation of the reduced oxide with H_2O is the sum of reactions 2.19 2.20.



The Gibbs free energy changes of reactions 2.19, 2.20 and 2.21 are shown on Figure 2.2b. Equations 2.19 and 2.20 are the reverse of the oxide reduction and water thermolysis reactions, and thus the oxide oxidation has a larger entropy change. The net reaction 2.21 is simply the difference in ΔG between the two reactions. It is most negative at the lowest temperatures, indicating that oxidation is thermodynamically most favorable at the lowest temperature possible. Effectively at these low temperatures the metal has a higher affinity for oxygen than H_2 does, as indicated by the more negative Gibbs energy at the lowest temperatures. However, as the temperature increases, the reverse is true and the oxidation becomes less favorable. Usually, the oxidation reaction is conducted at the highest temperature possible where thermodynamics is not hindered because of improved kinetics (i.e. more rapid reaction rates) and higher efficiencies are achieved because of smaller temperature swings between reduction and oxidation reactions that require a heat input. Efficiencies are a crucial matter for solar thermochemical redox-cycles. Siegel et al. [16] suggested

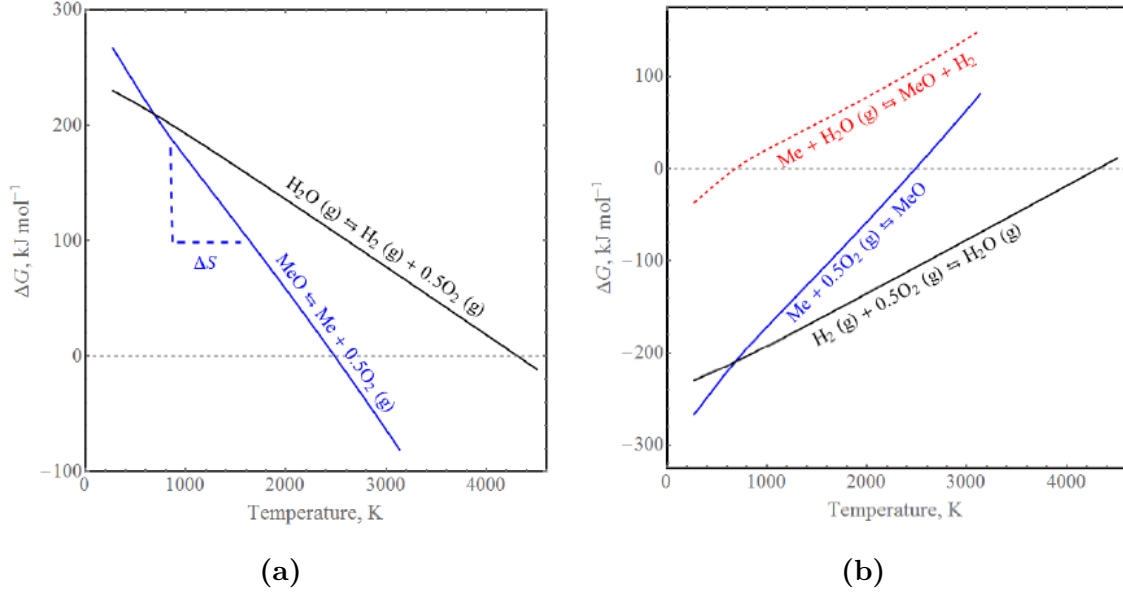


Figure 2.2: (a) Gibbs free energy change versus temperature of the water thermolysis reaction (black) and metal oxide reaction (blue). (b) Gibbs free energy change versus temperature of the metal oxide oxidation reaction with steam (dashed red), oxygen (blue) and H_2 oxidation (black).

that, when evaluated in comparison to H_2 production via photovoltaic coupled with electrolysis STC technologies need to achieve an annual average solar to fuel efficiency of at least 20% to be economically competitive. To date, the largest reported average solar-to-fuel energy conversion efficiency for STC CDS is 5.25% by Marxer et al. [17] using ceria (CeO_2) as the metal-oxide. CeO_2 is currently considered to be the state-of-the-art redox material because of its favorable oxidation thermodynamics, rapid reaction kinetics, and morphological stability. Despite its high regard, the fuel production efficiency achievable with CeO_2 and the practicality of its use are limited by the extremely high temperatures required for the thermal reduction step (1500 – 1600 °C, [18]). Higher operating temperatures imply larger energy penalties due to heat losses, place constraints on the materials of construction of the thermochemical reactor and results in extreme solar concentrator demands. To address the above mentioned limitations on the efficiency and operability, recent experimental and computational efforts have focused on the discovery of the new redox materials that operate at more moderate temperatures than CeO_2 while still retaining the thermodynamic favorability.

2.3 Solar redox materials

A main challenge for two-step thermochemical cycles is to develop a reactive material able to dissociate H_2O and/or CO_2 with fast reaction rate and performance stability over cycles. To be usable in solar-driven thermochemical cycles, a reactive material should thus satisfy most of the following criteria [19]:

- favorable thermodynamics for low reduction temperature ($< 1400^\circ C$);
- capacity to produce high amounts of H_2 and/or CO during oxidation step;
- fast kinetic rate;
- good thermal stability;
- low cost, non-toxicity, and largely availability.

There exist three distinct classes of metal-oxide redox pairs: (1) volatile stoichiometric, (2) nonvolatile stoichiometric, and (3) nonstoichiometric. In a volatile redox cycle, the temperature required for reduction is greater than the vaporization temperature of the metal-oxide, thereby causing it to undergo a solid-to-gas phase transition [10]. Some volatile redox pairs include ZnO/Zn and SnO_2/SnO . The practicality of large-scale implementation of volatile redox cycles is largely limited by the need for rapid quenching of the gas phase products. In nonvolatile stoichiometric and nonstoichiometric cycles, the redox intermediate remains in the solid phase throughout the reduction step. Nonvolatile stoichiometric reactions involve a change in crystal structure and the reduction of the cation to form solid compounds. Examples of nonvolatile stoichiometric redox pairs include Fe_3O_4/FeO . Stoichiometric reactions have a greater oxygen exchange capacity compared to that of nonstoichiometric reactions, however, they typically exhibit poor stability and slower reaction kinetics. From a thermodynamic perspective, large changes in entropy during oxygen exchange are desirable, as the entropy has a strong impact on the thermodynamic favorability and the temperature swing between reduction and oxidation. The solid-to-gas and crystallographic phase changes that occur during cyclic operation with the volatile and non-volatile stoichiometric redox pairs, respectively, are associated with larger changes in entropy than those of nonstoichiometric oxygen exchange. Nonstoichiometric reactions with metal-oxides such as CeO_2 and $LaMnO_3$ perovskites involve the partial reduction of the bulk metal-oxide, while maintaining the crystallographic structure. Similar to the ferrite system, doping schemes have been employed with CeO_2 and different perovskites to tune the thermodynamic parameters and redox performance.

2.3.1 Ceria (CeO_2)

Nonstoichiometric CeO_2 is regarded as the current state-of-the art in terms of STC redox performance due to several desirable thermodynamic and physico-chemical properties. It proceeds according to the reduction and oxidation reactions shown below:

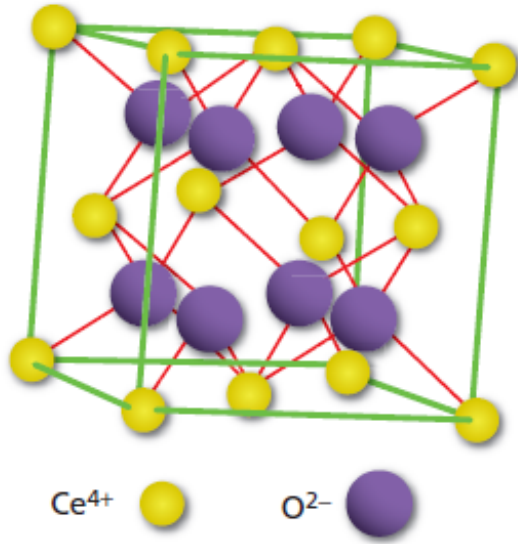
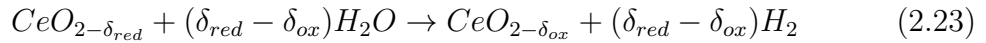
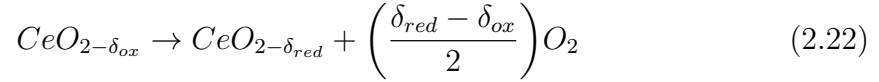


Figure 2.3: Cerium oxide lattice structure [3].

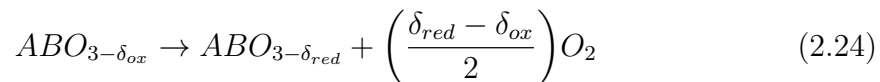
where δ_{ox} is the nonstoichiometry following oxidation and δ_{red} is the nonstoichiometry after reduction. Thus, their difference defines the amount of fuel capable of being produced per mol CeO_2 . In general, nonstoichiometry increases with increasing temperature and decreasing oxygen partial pressure (pO_2). Reduction of CeO_2 is typically performed at 1773 K and pO_2 between 10^{-6} and 10^{-3} atm, while the oxidation step is performed between 873 and 1273 K at pO_2 between 10^{-20} and 10^{-10} atm. CeO_2 has notably high entropy change associated with oxygen exchange when compared to other nonstoichiometric redox materials [20], leading to contained temperature swing (ΔT) between the reduction and oxidation steps and more favorable oxidation thermodynamics. It exhibits rapid reaction kinetics

and oxygen diffusion rates and shows exceptional resistance to sintering due to its high melting point. Furthermore, CeO_2 is able to maintain its cubic fluorite structure (Figure 2.3) during cycling over a wide range of operating conditions and reduction extents. However, during its relatively high enthalpy change during oxygen exchange [21], CeO_2 requires high operating temperatures in order to achieve

the higher efficiencies. Marxer et al. [15] demonstrated simultaneous extended WS and CDS redox cycles using the CeO_2 -based reticulated porous ceramic (RPC) with dual-scale porosities in cavity-type solar reactor. Over the course of 291 redox cycles, about 700 standard liters of syngas were produced, compressed, stored, and transported to Shell Global Solutions in Amsterdam and then catalytically processed via Fischer-Tropsch synthesis to produce the world's first solar-derived kerosene. The average energy conversion efficiency was 1.72%. Very recently, a solar-to-fuel energy conversion efficiency of 5.25% was achieved using the CeO_2 -based dual scale porous RPC in a second generation cavity reactor that improved the heat and mass transfer characteristics of the system [17]. Low energy conversion efficiency is currently hindering commercial, large-scale implementation of STC fuel production. Under idealized conditions, the incorporation of gas and solid-phase heat recovery was shown to offer a substantial improvement in efficiency which increased with increasing concentration ratio, when compared to operation with no heat recovery [22]. Large ΔT between the reduction and oxidation steps, particularly in the absence of solid-phase heat recovery, negatively impact the energy conversion efficiency and the cycle operability. This is because solar energy must be used to reheat the solid back to the reduction temperature, leading to an increase in energetic penalties, thermal stress in the reactor components, and cycle times.

2.3.2 Perovskites

Perovskites of the general form ABO_3 have recently been proposed as an alternative to CeO_2 for two-step STC fuel production in an effort to address the low reduction extents and high operating temperatures associated with its use. Perovskites have the general formula ABO_3 , where A and B are cations. The A cation is 12-fold coordinated with oxygen anion. Ideal perovskites present a cubic structure with space group Pm3m, as represented in Figure 2.4 [4]. Different elements can occupy the A and B sites of the perovskite according to their ionic radius. Due to the large number of dopant insertion options (27 possibilities for the A site and 35 possibilities for the B site), their composition can be tuned to optimize fuel production. The redox reactions occur according to Eqs. 2.24 and 2.25.



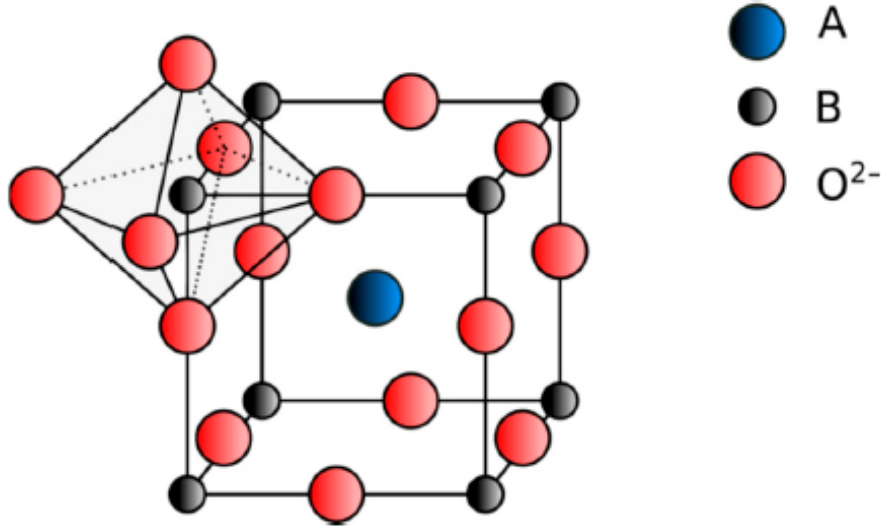


Figure 2.4: Ideal cubic perovskite structure with an octahedral site [4].

When compared to CeO_2 , perovskites show increased O_2 evolution during the high-temperature reduction step and a notable decrease in operating temperatures [23]. The larger deviation from stoichiometry provides a higher upper limit for fuel production. However, the oxidation reaction must be sufficiently favorable such that the reduced perovskite can fully replenish the oxygen lost during reduction. This is an issue for many of the perovskites that have been analyzed thus far, unless excess oxidant is used to increase the thermodynamic driving force [23] [20]. Scheffe et al. [16] introduced lanthanum-strontium-manganese (LSM) perovskites as a new class of solar redox materials for use in two-step STC WS and/or CDS. The reduction extent of these materials was about twice that of CeO_2 when reduced at 1773 K. Unlike CeO_2 , however, LSM materials could not be completely re-oxidized under any of the conditions investigated. Nonetheless, CO yields during CDS exceeded those of CeO_2 for the same operating conditions. Reduction extents of LSM-based perovskites at a particular temperature and pO_2 have been shown to increase with increasing Sr^{2+} content. However, this increase in reducibility is coupled with a decrease in WS and CDS favorability. The introduction of a divalent dopant on the A-site leads to a mixed Mn^{3+}/Mn^{4+} valence state, wherein higher Mn^{4+} content favors deeper reduction extents. Thermodynamically speaking, the partial molar enthalpy of reduction for LSM perovskites decreases monotonically with its increasing Sr^{2+} content, thereby decreasing the energetic penalties for reduction, while the entropy remains

relatively constant. Such a change in thermodynamic properties favors a decrease in operating temperatures, but leads to greater ΔT between redox steps. LSM-based perovskites exhibit notably lower enthalpies than CeO_2 providing further explanation for the higher operating temperatures required for the latter. The effects of a variety A-site doping schemes for $LaMnO_3$ perovskites on redox performance have been evaluated. These include: Sr^{2+} , Ca^{2+} , Ba^{2+} , Y^{3+} , La^{3+} , Nd^{3+} , Sm^{2+} , Gd^{2+} , and Dy^{2+} [24] [19]. In general, $La_{1-x}Ca_xMnO_3$ (LCM) perovskites have been shown to achieve deeper reduction extents than $La_{1-x}Sr_xMnO_3$ (LSM) perovskites [23] [21]. This is a consequence of their orthorhombic crystal structure, as opposed to the rhombohedral structure of LSM perovskites. Analogous to the trends observed for LSM perovskites, O_2 during reduction of LCM perovskites increases with increasing Ca^{2+} dopant concentration. Furthermore, LCM perovskites exhibit diminished oxidation favorability when compared to CeO_2 . The combination of A-site and B-site doping creates a large composition space in which the redox performance of perovskites may be tuned. With regards to STC fuel applications, most experimental and theoretical efforts have involved the study of $LaMnO_3$ perovskites with Sr^{2+} or Ca^{2+} A-site doping and Al^{3+} B-site doping. LSM- and LCM-based perovskites with Al^{3+} B-site doping (LSMA and LCMA) release more O_2 during reduction than CeO_2 and Al^{3+} free LSM- and LCM-based perovskites under comparable conditions [25] [23] [20] [21]. LSMA-based compounds exhibit notable improvements in fuel yields compared to CeO_2 , McDaniel et al. [25] observed 9- and 6-fold improvements in H_2 and CO yields, respectively. The oxidation kinetics have shown to be similar to those of CeO_2 and cyclical stability with on degradation or significant changes in redox performance has been demonstrated for up to 80 redox cycles (where reduction and oxidation were performed at 1623 and 1273 K, respectively). Despite Al^{3+} being redox inactive, its presence yields a notable effect on the redox performance of A- and B-site doped perovskites. Ezbiri et al. [20] investigated the surface activity of LSMA- and LCMA-based perovskites and determined that Al^{3+} doping on the B-site leads to $Mn^{2+/3+/4+}$ enriched surfaces. X-ray photoelectron spectroscopy (XPS) indicated that Mn is the only redox active metal on the surface. Enrichment of the perovskite surface with Mn is suggested to be the reason for the increased reduction extents of Al^{3+} doped LSM- and LCM-based perovskites in comparison with their respective Al^{3+} free counterparts. Moreover, Mn-enrichment of the surface of LSMA-based perovskites is accompanied by Sr^{2+} depletion. Thus, these perovskites show a decreased tendency to form carbonates, which has been observed experimentally by Cooper et al. [23] and Galvez et al. [26]. The partial molar thermodynamic properties of $LaMnO_3$ perovskites with Sr^{2+} or Ca^{2+} A-site doping and Al^{3+} B-site doping have been determined [23] [20] [21]. In general, most LSM- and LCM-based

perovskites with Al^{3+} doping have partial molar enthalpies that decrease with increasing nonstoichiometry, as opposed to Al^{3+} free LSM and LCM perovskites whose enthalpies increase as the deviation from stoichiometry increases. Furthermore, the partial molar enthalpies and entropies of LSMA and LCMA perovskites are generally lower than those of CeO_2 . The diminished enthalpy values are responsible for the perovskites greater reduction extents at lower temperatures (due to a downward shift in the Gibbs free energy change). In terms of oxidation thermodynamics, Ezbiri et al. [20] showed that the oxidation of CeO_2 is notably more favorable than that of the LSMA-based perovskites (while having the lowest reduction favorability).

Chapter 3

Experimental Tests

3.1 Experimental Setup

3.1.1 Microreactor Setup Description

Most of the aforementioned studies make use of an experimental setup based on Thermogravimetric Analysis (TGA). However, one of the primary alternative methods for studying redox materials involves using a microreactor setup. In a TGA setup the measured quantity is the mass variation of the sample, while in a microreactor setup it is possible to directly measure the products of the process by means of a gas analyzer. Both setups have advantages and disadvantages, for instance, the mass variation in the TGA can be influenced by the formation of unwanted species such as carbonates, while in the microreactor the carbonates formation does not influence the measurements. On the other hand, the TGA allows to study more in depth the extents of reduction and oxidation of the material, while a microreactor does not provide enough information to do so. Nevertheless, the two methods are complementary and the data obtained from both are necessary to adequately outline the material behaviour and its properties. The test bench - Figure 3.1 - used for this analysis is installed at the Environment Park's CO_2 Cycle Lab. The bench is equipped with a feeding system consisting of 7 gas lines and a water vapor generation system. There are 5 gases supplied through the laboratory lines, N_2 , CH_4 , CO , CO_2 and H_2 , while further gas cylinders can be plugged to the 2 remaining lines. Each line is equipped with a mass-flow controller (MFC) which can adjust the mass-flow rate between 10 and 500 Nml/min . The gas pipelines then converge into the dry mix line, which in turn is connected to the microreactor through a three-way valve. It is possible to

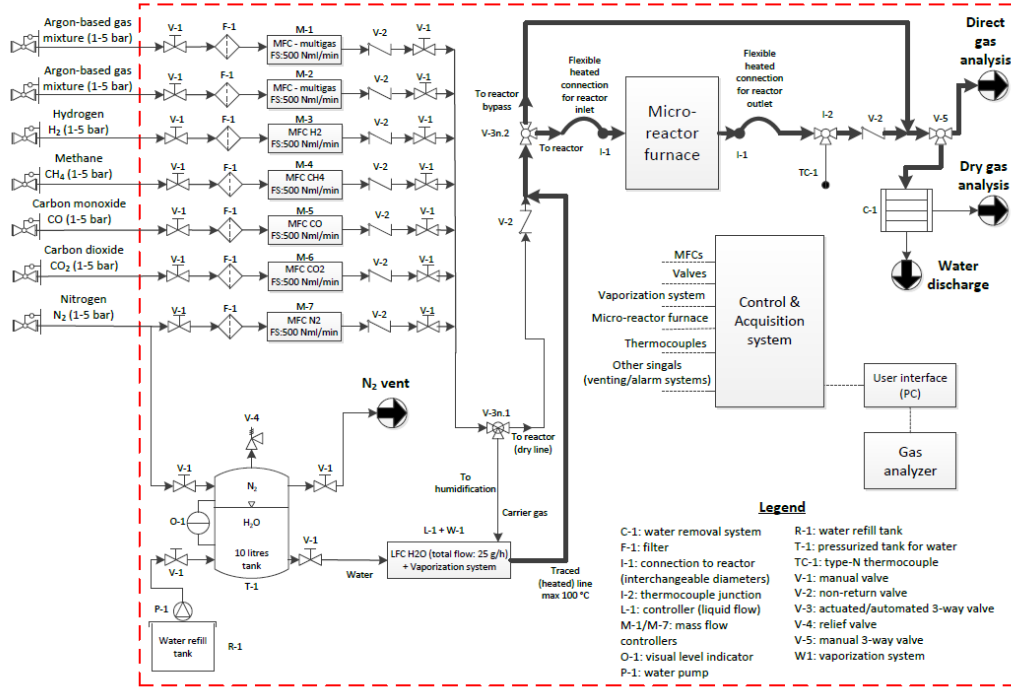


Figure 3.1: Schematic of the test bench

directly feed the microreactor or to bypass it. At the end of the line there is the continuous gas analyzer. The microreactor consists of a ceramic tube heated by an electric furnace (Carbolite Gero). The multichannel gas analyzer is able to measure the concentration of the gases contained in the microreactor's output stream.

Microreactor

The microreactor is the main component of the test bench, it contains a ceramic tube inside which the material reacts with the inlet stream of gases. The tube is made of alumina - Al_2O_3 -, it is 1 m long and has an internal diameter of 32 mm. The temperature inside the tube is controlled by an electrical power supply - Figure 3.2 - through its own software, the material is held in place by an alumina crucible (Figure 3.3).

Gas Analyzer

In this experimental setup, the Emerson Rosemount X-Stream XE gas analyzer has been employed. It works with conditioned gas mixtures only, meaning that the gas stream has to be dry, dust-free, and free of any components which may damage the instrument. For this reason, upstream the gas analyzer there is a condenser that removes the moisture from the gas flow which comes from the microreactor. The multichannel gas analyzer allows to separate the measurement of five distinct chemical species, CO_2 , H_2 , CH_4 , O_2 and CO .



Figure 3.2: Schneider Electric power supply



Figure 3.3: Alumina crucible

3.2 Experimental Tests and Results

$La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}$ is the material investigated in this work. The goal is to verify that the sample of the material actually works and behaves consistently with what is reported in literature and then perform CO_2 -splitting cycles in order to extract a yield of the material (micromoles of CO produced per gram of material).

3.2.1 Test 1

In this test, the thermochemical CO_2 splitting reactivity of the powder was studied in the microreactor, a 10 mg sample was used. The temperature was first increased to $1400^\circ C$ with an heating rate of $20^\circ C/min$ and 500 ml/min of nitrogen was supplied. After 30 min plateau at $1400^\circ C$, during which the reduction takes place, the temperature was decreased to $1050^\circ C$ with a cooling rate of $5^\circ C/min$. An equimolar mixture

of CO_2 and N_2 ($250\text{ ml/min } CO_2$ and $250\text{ ml/min } N_2$) was then introduced in the system to perform the the oxidation step, which lasted 5 min. The temperature was increased again to $1400^\circ C$ under nitrogen and the CO_2 splitting cycle was operated for 11 more times. Figure 3.4 shows the temperature and the gas flows programs of the test while Figure 3.5 shows the results in terms of measured CO concentration (in ppm). The peak of CO production decreases as the number of cycles increases until it reaches a plateau. It is necessary to calculate the production yield of each cycle and compare it with the values from literature [19]. As we can see from Figure 3.6, the CO production peaks around 40 s after the start of the oxidation process and then settles down at 100 ppm. The measured 100 ppm after the peak are not real, because they continue to be present even when no CO_2 is introduced. Thus, it is necessary to adopt a criteria to correct the curve because, otherwise, the yield calculated as the integral of said curve would be definitely overestimated. A straight line has been drawn from the origin to the point where the slope of the curve is smaller than 0.05 % - Figure 3.7 - and the adjusted curve has been defined by subtracting the line's values from the original curve ones - Figure 3.8 -. Figure 3.9 shows the CO production curves of the subsequent cycles, it may be noted that the peaks and duration of the cycles decrease as the number of the cycles increases possibly due to a thermal stabilization of the fresh sample. The cycle yield (micromole produced per gram of material) is the area under the CO production curve and is computed as the integral of said curve. This procedure has been repeated for all the 12 cycles, results are reported in Figure 3.10. The yield decreases progressively (following the cycles peaks) and seems to plateau around $200\text{ }\mu\text{mol/g}$, which is the value reported in literature [19]. While one would think that the material has stabilised and behaves coherently with what has already been found, that is not necessarily the case. The sample recovered from the furnace had decreased its mass, probably due to some kind of reaction with the alumina crucible. At this point, it is not possible to assess if the reduction of the yield is due to a material stabilization or to its mass decrease. For this reason, further TGA tests were carried out in order to be able to use a platinum crucible which should be less likely to react with the sample.

3.2.2 Test 2

With this test, the stability of the material over a relatively large number of cycles wants to be assessed. Around 25 mg of material were used, 20 cycles similar to the cycles of the Test 1 were performed. A stabilization step at 873 K was added in order to have a reference weight for extracting the oxygen non-stoichiometry. The difference between the thermogravimetric analysis and the microreactor setup is that

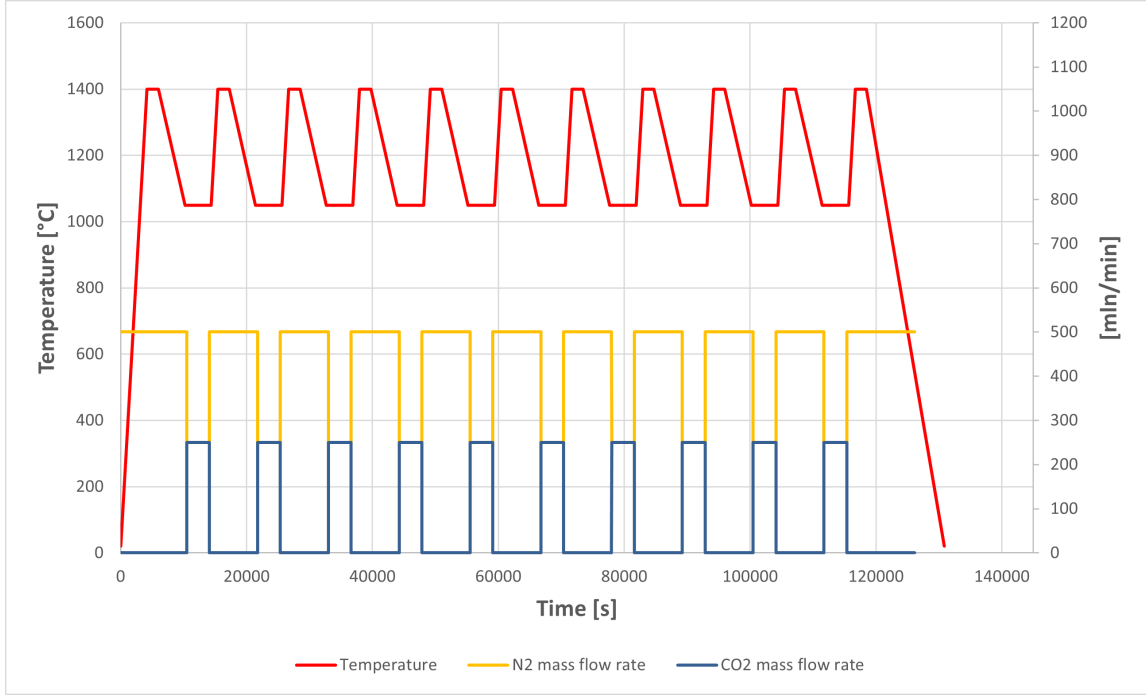


Figure 3.4: Temperature and gas flows programs of 12 CO_2 splitting cycles

the measured quantity is not the amount of CO produced but rather the variation of the mass of the sample through the test. The cycles' yield is then computed as follows:

$$Y = \frac{\Delta m_s}{m_{LSMA} M_O} \quad (3.1)$$

where Δm_s is the relative weight loss in a cycle, m_{LSMA} is the mass of the sample and M_O is the molar mass oxygen. Figure 3.11 shows the temperature program and the mass variation of the sample over 20 cycles. Besides the first cycle, which shows a greater extent of reduction, there is no significant difference between the shape of the curves of subsequent cycles, thus indicating that the yield reduction observed in Test 1 was probably due to a progressive drop of the reacting sample's mass. The yield calculated with Equation 3.1 is reported in Figure 3.12. It fluctuates around $240 \mu mol/g$ with minimal deviations except for 2 cycles out of 20, the results are consistent with literature [19] and no progressive decrease in yield is observed.

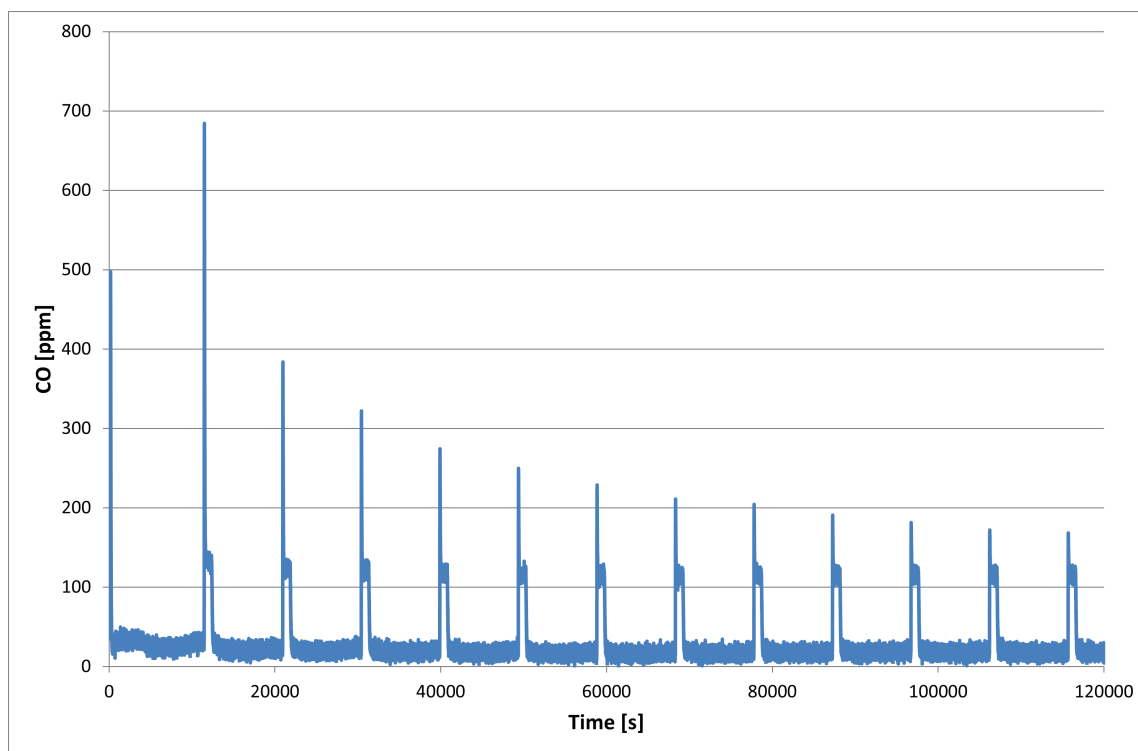


Figure 3.5: Measured CO production of 12 CO_2 splitting cycles

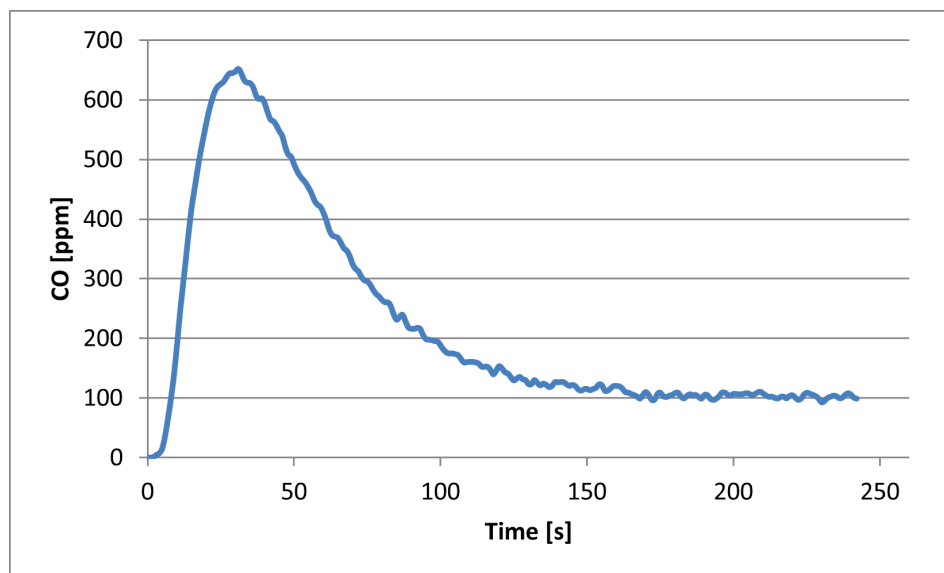


Figure 3.6: CO production of a single cycle

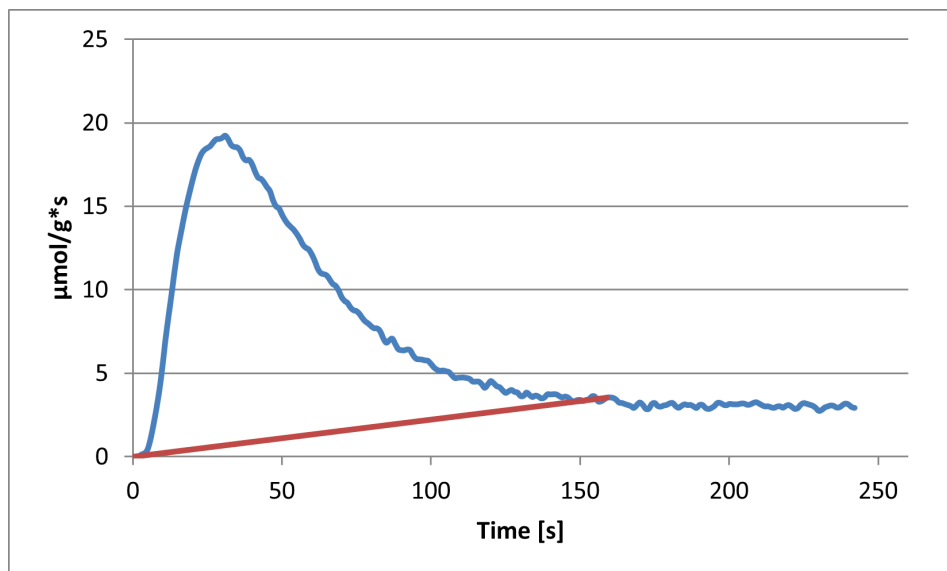


Figure 3.7: Correction line

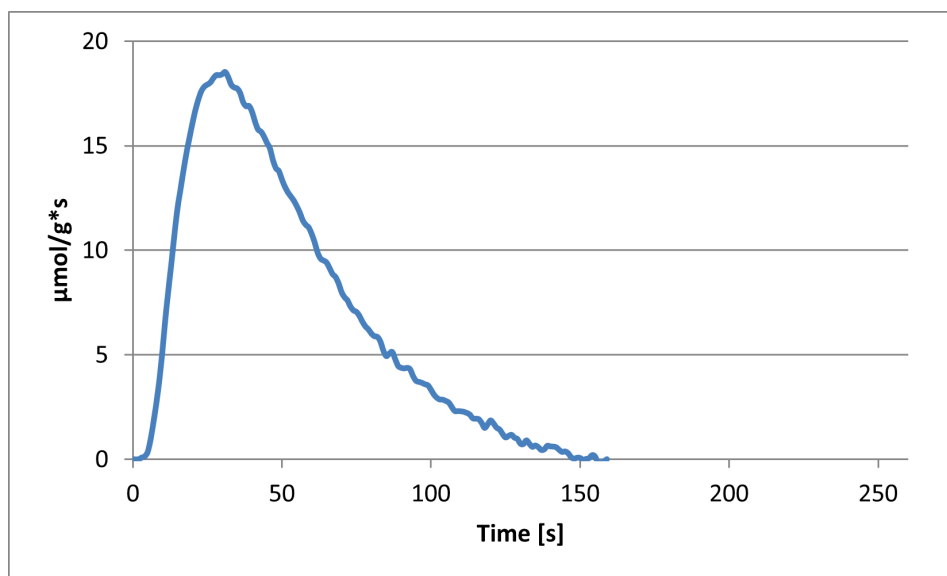


Figure 3.8: Corrected CO production curve

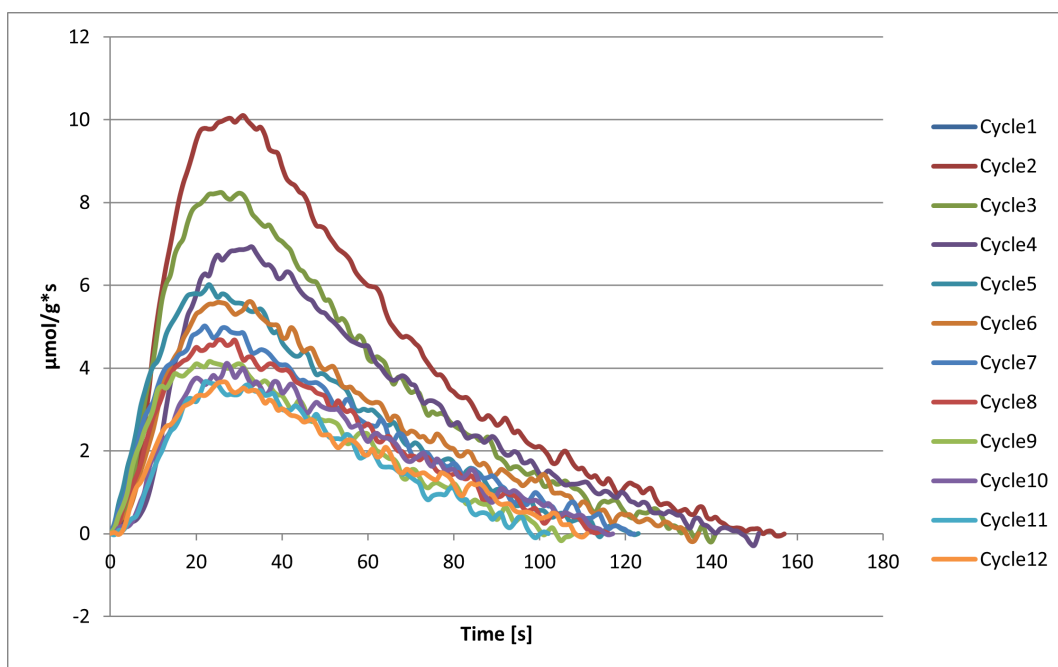


Figure 3.9: Corrected CO production curve of subsequent cycles

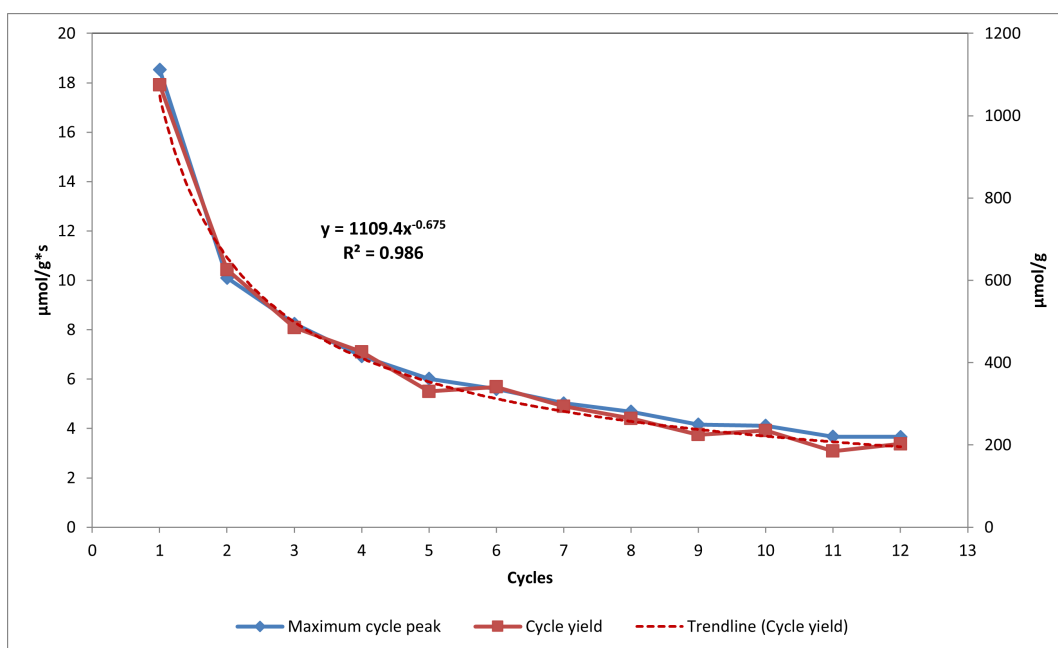


Figure 3.10: Corrected CO production curve of subsequent cycles

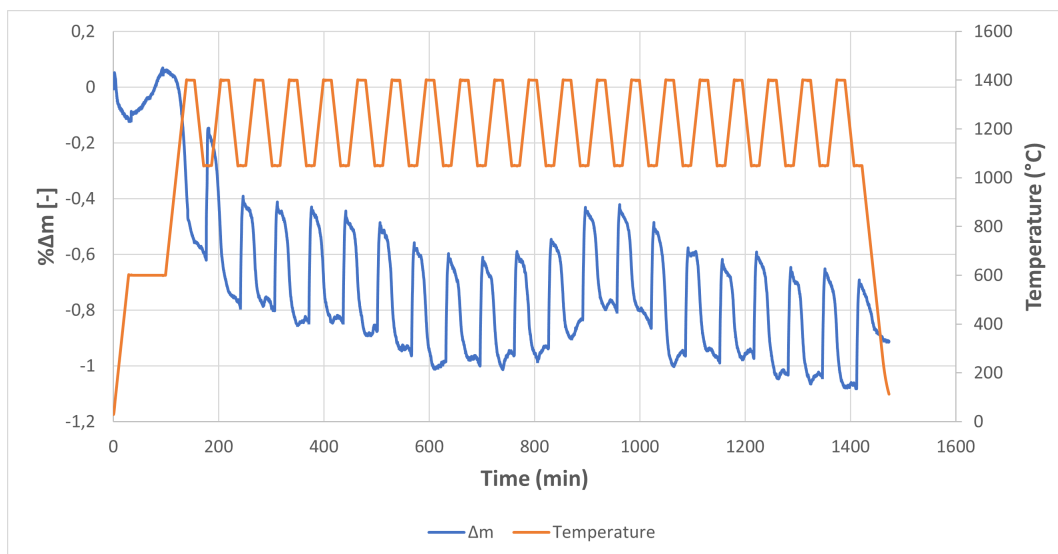


Figure 3.11: Temperature program and mass variation of the sample over 20 cycles

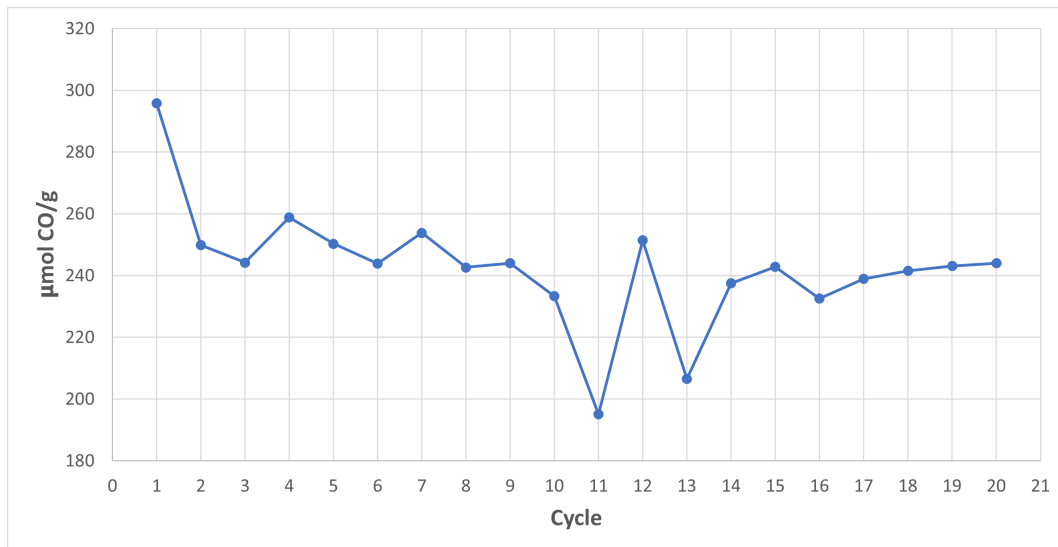
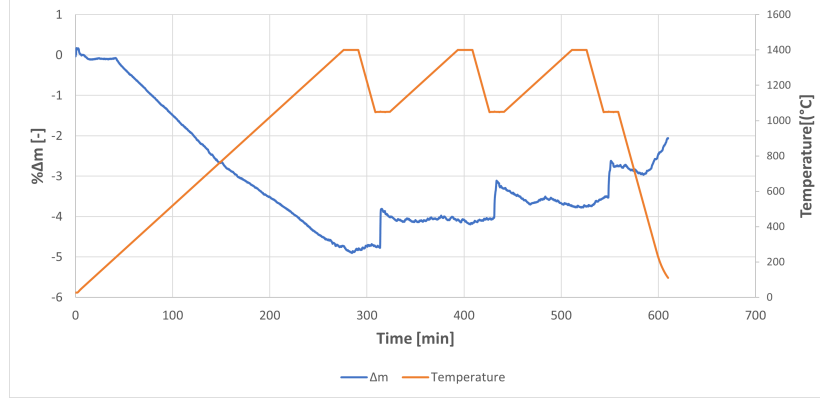


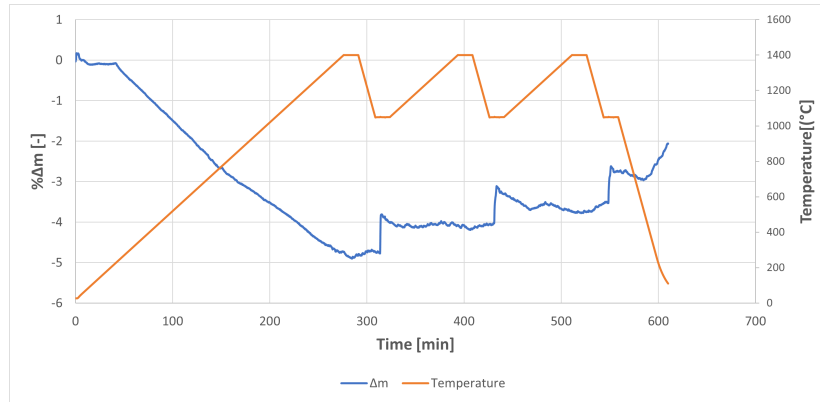
Figure 3.12: Yield of 20 consecutive cycles

3.2.3 Test 3

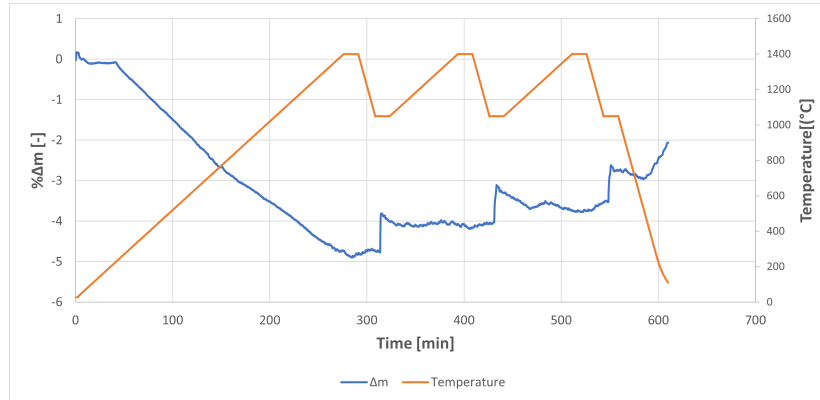
The aim of this test was to investigate the influence of the heating rate during the heating ramps. For this reason, 3 cycles similar to that of Test 1 were performed and the heating rate was varied between $5^{\circ}\text{C}/\text{min}$, $10^{\circ}\text{C}/\text{min}$ and $20^{\circ}\text{C}/\text{min}$. Figures 3.13a, 3.13b and 3.13c show the temperature program and the mass variation of the sample. It is possible to notice that, with an heating rate of $5^{\circ}\text{C}/\text{min}$ and $10^{\circ}\text{C}/\text{min}$, the mass of the sample struggles to go back to its original value after the first cycle. Instead, with an heating rate of $20^{\circ}\text{C}/\text{min}$, the three cycles are approximately the same, suggesting that an heating rate of $20^{\circ}\text{C}/\text{min}$ may be a better choice. The assumption is confirmed by the data of the computed cycles yield (Figure 3.14). They show that the yield of the cycles where an heating rate of $10^{\circ}\text{C}/\text{min}$ is used is lower than the one of the cycles with an heating rate of $20^{\circ}\text{C}/\text{min}$, so there is no point in using such value. As to the heating rate of $5^{\circ}\text{C}/\text{min}$, it results in a slightly higher yield that yet does not justify the higher demand of energy required to heat the sample at a much slower rate. Therefore, an heating rate of $20^{\circ}\text{C}/\text{min}$ has been confirmed as the more appropriate value.



(a)



(b)



(c)

Figure 3.13: (a) Gibbs free energy change versus temperature of the water thermolysis reaction (black) and metal oxide reaction (blue). (b)

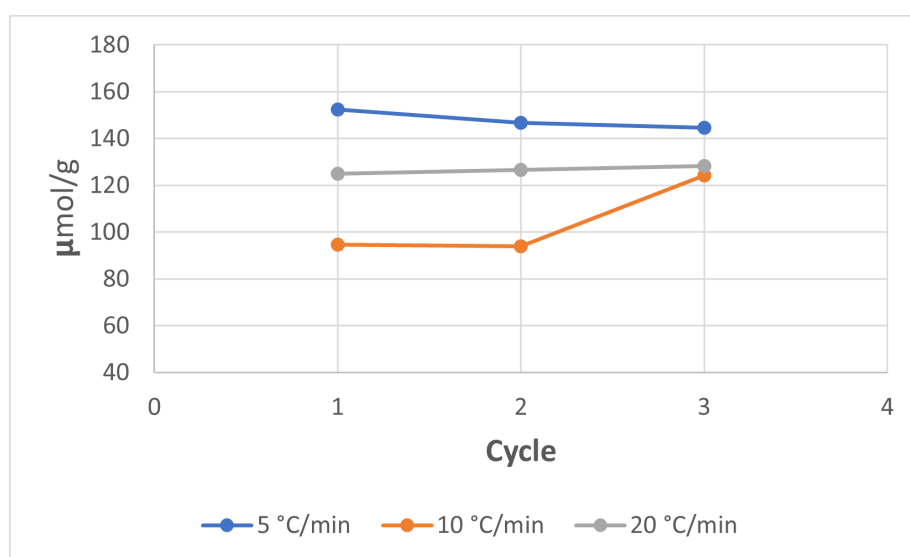


Figure 3.14: Yield of the cycles with different heating rates

Chapter 4

Process Simulation

4.1 Simulation description

In this section, the results from the experimental tests are used to model a chemical looping process with a simulation software in order to calculate an efficiency. The software used for the simulation is Aspen Plus®, a chemical process simulator widely used for chemical engineering applications. As previously discussed, the experimental setup used in the tests worked in batch conditions, the material was stationary inside the reactor and was cyclically exposed to different gases. While this setup can be convenient for a laboratory environment, it may be difficult to implement it in a process simulation software (and in an actual plant as well). For the sake of calculating an efficiency of the process, a simpler configuration is sufficient. The system has been configured to work in stationary conditions with a constant production rate, it is modeled with two reactors, one for the reduction phase and one for the oxidation phase, the oxygen carrier material is transported between the two and cycled back. A schematic of the model is shown in Figure 4.1.

4.2 Reactor choice

A reactor which utilizes the movement of particles is called non-structured reactor. The movement of the OC enables the easy decoupling between the oxidation and reduction reactor, which often have dissimilar reaction kinetics. The most common reactors of this category are fluidized bed and moving bed reactors. In a fluidized bed reactor, an inert gas is required as sweep gas to carry away the oxygen released

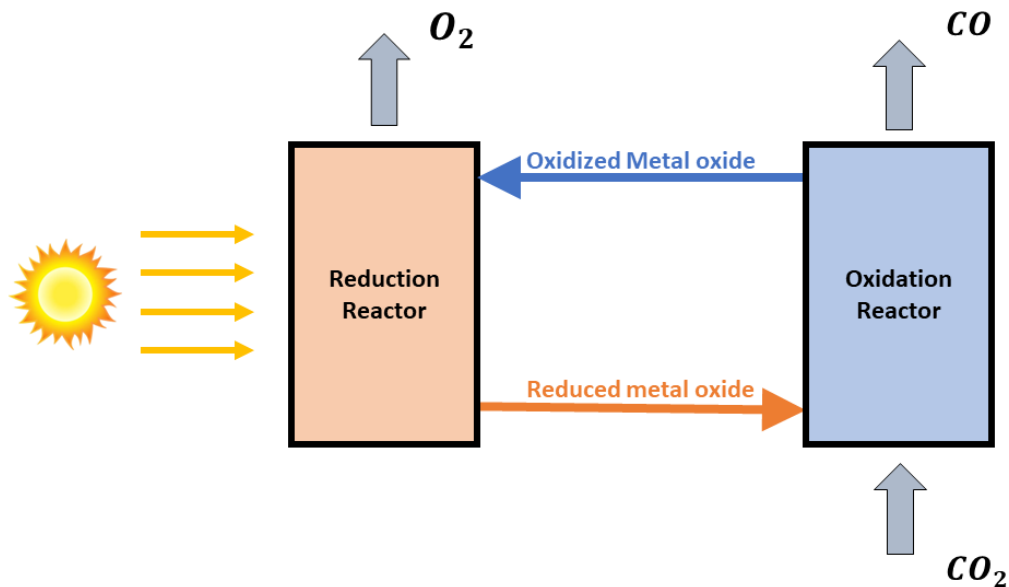


Figure 4.1: Schematic of the modeled redox reactors system.

during the reduction process and maintain a very low partial pressure of oxygen. In order to maintain an oxygen partial pressure of around $10^{-5} atm$, which would be ideal to reach large values of non-stoichiometry [27], a very high volume of sweep gas of the order of 10^5 times would be needed [28], making it very energy intensive and require a large volume of the reduction reactor. Moreover, the huge volume of inert gas would severely limit the subsequent separation of the oxygen. In a moving bed reactor, instead, the OC material is carried with a mechanical system and the released oxygen is removed by means of a vacuum pump coupled with the reduction reactor. This, and others features related to the ease of control of the residence time of the OC inside the reactor [29, 30], make the moving bed reactor the most suitable for industrial size STC applications for both reduction and oxidation steps. Therefore, the choice fell on a moving bed reactor for this work.

4.3 Model description

In the Aspen Plus® software, two stoichiometric reactors are used for the reduction and oxidation phases. The conversion of the reactants is defined, the totality of the OC material takes part in the reduction reaction and in the oxidation reaction, while only a percentage of the total CO_2 , correspondent to the amount necessary to fully

oxidate the OC, takes part in the oxidation reaction in the oxidator. A schematic of the Aspen Plus® model is shown in Figure 4.2, it consists of the following components:

- LSMHEAT. A heat exchanger to heat the oxygen carrier, it increases the temperature from 1050°C , which is the temperature at the exit of the oxidation reactor, to 1400°C , which is the reduction temperature of the Test 2 taken as reference. In an actual system, this component would not be present, because the task of heating the solid material is responsibility of the reactor itself. However, in order to be able to discern the power needed to increase the temperature from the power needed to drive the reaction, it has been decided to employ a further reactor in the simulation.
- RED. The stoichiometric reduction reactor, it receives the fully oxidized LSMA stream as input and reduces it upon heating.
- SEP. A separator used to remove the oxygen from the stream. The separator is added in the model because the component "RStoic", that models a stoichiometric reactor in Aspen Plus®, only allows for one outlet stream. A real moving bed reactor would have two different outlets, one for the solid and one for the gas - which would be extracted by means of a vacuum pump -. The same consideration applies for the separator SEP2, downstream of the oxidation reactor.
- COOLER. A heat exchanger to cool down the reduced LSMA from 1400°C to the oxidation temperature, 1050°C .
- CO2HEAT. A heat exchanger to heat the CO_2 from the ambient temperature to the oxidation temperature.
- OXI. The stoichiometric oxidation reactor, it receives the reduced LSMA and oxidize it with a CO_2 stream, thus producing CO .
- SEP2. A separator used to remove the LSMA from the gas stream.
- SEP3. A separator used to remove the CO from the CO_2 stream. This separator would actually be present in the system, unlike SEP and SEP2.

The simulation computes the thermal powers exchanged by the heaters and the reactors for the given conditions of temperature and flow rates. The thermal powers of the reactors only consider the heat of reaction and do not include thermal losses. In addition, the pressure losses are not included, with all the components working at 1 bar. Before starting the simulation, the software requires an equation of state for

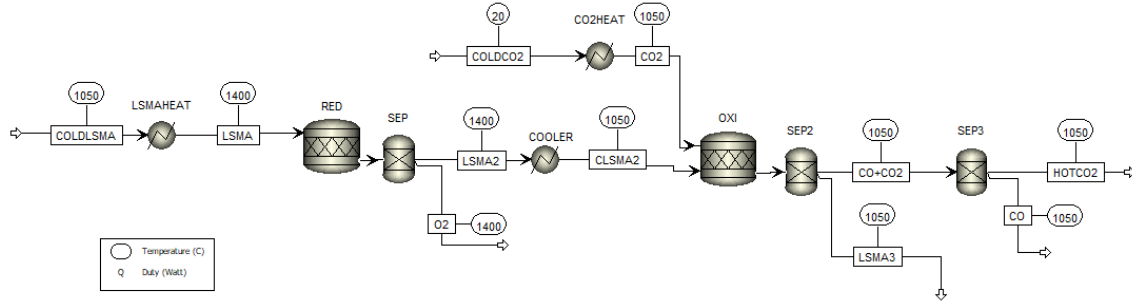


Figure 4.2: Schematic of the system.

the gases. For this work, the Peng-Robinson equation of state is used. Unlike the ideal gas law, the Peng-Robinson equation is cubic (as it can be written as a cubic function of the gas volume) and has additional parameters related to the critical properties and the acentric factor of a specific gas [31]. The acentric factor is a conceptual measure of the non-sphericity of a molecule. Now that the structure of the model has been defined, the issue of representing the material in the simulation needs to be addressed. As LSMA6464 is not present in the software's libraries, it was modeled as a mixture of metal oxides, namely La_2O_3 , SrO_2 , Mn_2O_3 and Al_2O_3 . Ezbiri et al. [20] performed X-Ray photoelectron spectroscopy (XPS) of LSMA-based perovskites and determined that Mn is the only redox active metal on the surface. Therefore, among the different metal oxides, Mn_2O_3 is the only one that actually goes through the redox reaction (4.1).



Mn_3O_4 releases oxygen in air at temperatures above $899^\circ C$ and Mn_3O_4 takes up oxygen at lower temperatures [32]. These temperatures are lower than the temperatures employed in the Test 2, therefore Mn_2O_3 has been chosen as reacting oxide among the other Mn oxides. In the Test 2, the sample mass was 24.623 mg , corresponding to $1.17 \cdot 10^{-4} \text{ mol}$, and the average oxygen production was 0.10208 mg per cycle, corresponding to $3.174 \cdot 10^{-6} \text{ mol}$. From Equation 4.1, 6 moles of Mn_2O_3 are needed to produce one mole of molecular oxygen, therefore, it is possible to calculate the moles of Mn_2O_3 needed to produce the same amount of oxygen of a mole of LSMA:

$$\frac{3.174 \cdot 10^{-6} \text{ mol } O_2}{1.17 \cdot 10^{-4} \text{ mol } LSMA} \cdot 6 \frac{\text{mol } Mn_2O_3}{\text{mol } O_2} = 0.1625 \frac{\text{mol } Mn_2O_3}{\text{mol } LSMA} \quad (4.2)$$

Consequently, 1 *mol* of LSMA6464 has been modeled as 0.5958 *mol* of an oxides mixture with the following mass fractions:

- 0.2727 La_2O_3
- 0.2727 SrO_2
- 0.2727 Mn_2O_3
- 0.1819 Al_2O_3

Another important parameter of the simulation is the ratio between the moles of CO_2 and the moles of $LSMA$ - n_{CO_2}/n_{LSMA} - during the oxidation phase. The oxidation phase in the Test 2 lasted 5 *min* and a stream of 120 *ml/min* of CO_2 and 120 *ml/min* of Ar was supplied. Therefore, $n_{CO_2}/n_{LSMA} = 166$, being the amount of $LSMA$ $1.17 \cdot 10^{-4} \text{ mol}$. The simulation has then been launched with 1 *mol/min* of $LSMA$ and 166 *mol* of CO_2 .

4.4 Simulation results

The results of the simulation are shown in Figure 4.3. The temperature of each stream in $^{\circ}C$ and the thermal power in *W* exchanged by each component are displayed. The values of the outputs in *kW* are displayed in Table 4.1.

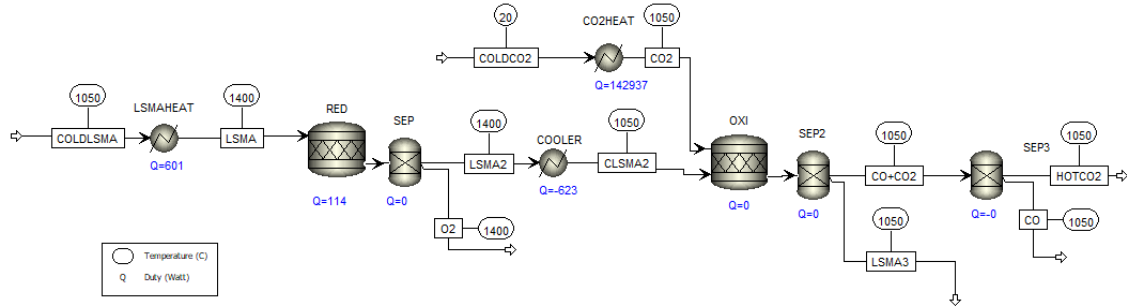


Figure 4.3: Results of the simulation.

The heat duties represent the heat flows absorbed by the components when positive and the heat flows released to the external environments when negative. The energy

Simulation	1
Reduction Temperature [$^{\circ}C$]	1400
Oxidation Temperature [$^{\circ}C$]	1050
$Q_{LSMAHEAT}$ [kW]	0.601
Q_{RED} [kW]	0.114
Q_{COOLER} [kW]	-0.623
$Q_{CO2HEAT}$ [kW]	142937

Table 4.1: Heat duties of the heaters and reactors

needed to heat up the CO_2 takes up the bulk of the energy consumption because of the high ratio between moles of CO_2 and moles of $LSMA$. This is common in chemical looping cycles with perovskites as oxygen carriers, because of the large excess of oxidant required to fully reoxidize these specific class of material. Similar results were obtained by Wang et al. [33], who performed chemical looping cycles employing an LCZ-73 perovskite as oxygen carrier. Considering that only a small amount of CO_2 participates in the oxidation process, the exhaust gas downstream the oxidation reactor carries a large amount of heat that can be used to preheat the CO_2 required for the oxidation reaction. This operation can be performed with a heat exchanger whose coefficient, ϵ_{he} , can be chosen equal to 0.75 [34]. The oxidation reaction is usually exothermic, meaning that heat is released to the environment at the oxidation reactor thus improving the process efficiency if recovered. However, due to the uncertainty related to the simulation of the behaviour of the material, it has been decided to not consider this contribution in order to avoid overestimating the efficiency of the process.

4.4.1 Efficiency of CO production

The efficiency of the process is defined as the ratio between the useful energy that can be extracted from the fuel and the energy spent to carry out the fuel production process. The useful energy Q_{CO} is the energy content of the produced carbon monoxide, and is obtained as:

$$Q_{CO} = \dot{n}_{CO} \cdot HV_{CO} \quad (4.3)$$

$\dot{n}_{CO}$ is the molar flow rate of CO in mol/s and HV_{CO} is the CO molar heating value, equal to 282.5 kJ/mol . The spent energy is the sum of of the heat duties of the

various components in the Aspen Plus® model and the work of the vacuum pump. A vacuum pump is needed to eliminate the residual air in the reactor to provide a lower oxygen partial pressure environment during the thermal reduction process. Oxygen partial pressure has a significant impact on the efficiency of the process, and it is common to maintain it at values around 10^{-5} atm . Bhosale [27] found that decreasing the oxygen partial pressure from 10^{-1} atm to 10^{-5} atm can decrease the non-stoichiometry, and consequently the efficiency, of approximately 6-fold. The ideal pump work is used to calculate process efficiency.

$$Q_{pump} = \dot{n}_{O_2} R T_{pump} \ln(p_0/p_{O_2})/\eta_S \quad (4.4)$$

where $\dot{n}_{O_2} = \dot{n}_{CO}/2$ follows from the reaction 2.18 stoichiometry, R is the universal gas constant, T_{pump} is the operating temperature of the pump. In this work, the temperature is the ambient temperature, p_0 is the atmospheric pressure and p_{O_2} is the oxygen partial pressure inside the reduction reactor after vacuuming, η_S is the solar energy to pump work conversion efficiency and its value is assumed to be 0.1 [33]. The process efficiency can then be expressed as follows.

$$\eta = \frac{Q_{CO}}{Q_{LSMAHEAT} + Q_{RED} + (1 - \epsilon_{he})Q_{CO2HEAT} + Q_{pump}} \quad (4.5)$$

The flow of oxygen extracted at the reduction reactor is equal to $4.51 \cdot 10^{-4} \text{ mol/s}$, the flow of CO produced at the oxidation reactor is equal to $9.02 \cdot 10^{-4} \text{ mol/s}$. Consequently, the overall efficiency of the process is equal to 0.7%. This number is consistent with what has already been found in literature, Wang et al. [33] obtained an efficiency of 1.36% with 75% heat recovery on a chemical looping process performed with an LCZ-73 perovskite. However, there are some factors indicating that the process efficiency may have been underestimated in this work. The experimental test which the simulation refers to, Test 2, was performed with inert gas sweep, which, as previously discussed, is not the optimal solution. Consequently, it was not possible to accurately control the oxygen partial pressure inside the reduction environment, previous experiments performed in the same test bench also suggested that minor air leaks may be present in the gas supply line. Therefore, the non-stoichiometry of the cycles has most likely been hindered by the undesired oxygen presence during the reduction phase. Moreover, the oxidation phase was performed without varying the mass flow rate of the CO_2 and with an equimolar mixture of Ar and CO_2 instead of pure CO_2 . Therefore, the $CO_2/LSMA$ ratio of 166 may be an overestimation and the effect of reducing the $CO_2/LSMA$ ratio has not been

assessed. Further tests need to be performed with a better tuning of the oxygen partial pressure during the reduction phase and by varying the CO_2 excess. The simulated process can help understand how the efficiency would vary if it was possible to reduce the $CO_2/LSMA$ ratio without hindering the non-stoichiometry of the perovskite. Three cases were considered, $CO_2/LSMA$ ratio reduced of 10 %, 25 % and 50 %, results are shown Table 4.2 and Figure 4.4.

Simulation	2	3	4
n_{CO_2}/n_{LSMA}	150	125	83
Q_{CO_2HEAT} [kW]	129160	107633	71468
η [%]	0.78	0.92	1.36

Table 4.2: Heat duties of the CO_2 heating reactor.

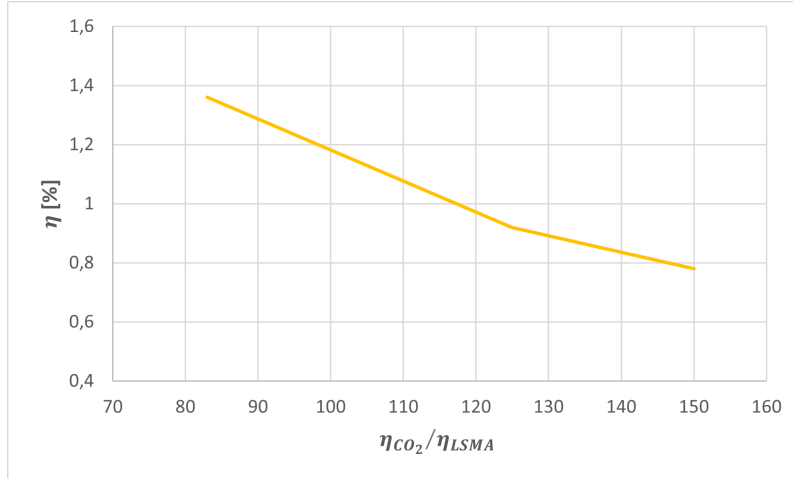


Figure 4.4: Efficiency variation.

By reducing the $CO_2/LSMA$ ratio of 50%, it is possible to reach an overall efficiency of 1.36%, and, based on what has previously been discussed, it is not an unrealistic goal. Moreover, lowering the oxygen partial pressure during the reduction phase would eventually further increase the efficiency.

Chapter 5

Conclusions

The aim of this work is to present experimental and simulation studies on a perovskite material, $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_3$ (LSMA), and discuss the possibility of using an experimental setup consisting of a microreactor and a gas analyzer, rather than the widely used TGA. The LSMA perovskite can operate in a two step chemical looping process to produce fuels from either CO_2 or H_2O , this work focuses on CO_2 -splitting cycles therefore CO is the fuel of interest. The microreactor setup proved to be a viable option to perform chemical looping cycles, compared to the TGA it allows the use of much bigger samples of material, even in the range of grams if necessary, whereas the TGA can only manage a few tens of milligrams. Moreover, in the microreactor it is possible to circulate a larger flow-rate compared to the TGA, up to 500 ml/min per gas, which is the limit imposed by the MFC on the gas supply line. Instead, in the TGA, the limit on the flow-rate is different for each gas, a common value is 240 ml/min but some gases, like CO_2 , are limited to 120 ml/min . Therefore, the microreactor setup is a more flexible option if the influence of extensive parameters like the mass of the sample or the flow-rate want to be explored. However, it is necessary to solve some issues related to the use of this specific instrument. For instance, the mass reduction experienced during the Test 1 needs to be further investigated. Its root cause is probably a reaction of the material with the alumina crucible, so it may be useful to try to use a different holder, but other reasons need to be excluded as well. It is possible that the powder is carried away by the gas flow, in this regard a tube-in-tube configuration can be employed. With this setup, the material is located inside a hollow pipe through which the gas can flow, and kept in place by two quartz wool elements which would serve as mechanical trap in the event of excessively high flow-rates. Other issues related to the gas analyzer are the difficulty to measure low concentrations of O_2 , which is a crucial metric if the

reduction extent in relation to the oxygen partial pressure wants to be investigated, and the influence of the flow rate on the measurements of some gases. To conclude, if properly tuned, the microreactor setup can certainly enhance the investigation possibilities provided by the TGA. In this work, tests on both the microreactor and the TGA were performed due to the inability to fully rely on the microreactor.

The experimental tests showed results consistent with what has already been found in literature for perovskites used in chemical looping cycles. In Test 1, the cycle yield plateaued around $200 \mu\text{mol/g}$ after some stabilization cycles, and this value has already been produced by other experimental campaigns. This test was performed at a reduction temperature of 1400°C , which is already lower than the temperatures used in chemical looping cycles where ceria is used as oxygen carrier ($1500 - 1600^\circ\text{C}$), but it would be interesting to investigate lower reduction temperatures with the aim of reducing both the maximum temperature reached in the cycle and the temperature swing between reduction and oxidation (this one performed at 1050°C). In Test 2, an average net mass reduction of 0.4% was obtained over 20 chemical looping cycles. This value is slightly lower than other results found in literature (0.7%), and the reason is probably due to the fact that in most experimental works, spherical samples with custom made crucibles were used, thus enhancing the surface exposed to the gas flow. In this work, a commercial crucible was used and only the upper surface of a cylinder was exposed to the gas flow. To date, there are no scientific papers that focus specifically on the influence of the heating rate on the cycle yield or on the efficiency of the process, but in Test 3, $20^\circ\text{C}/\text{min}$ was confirmed to be the optimal value, which is already employed in most experimental works.

In the last part, a theoretical efficiency of the CO production process was computed by means of commercial software Aspen Plus® and data from Test 2. Results showed that the bulk of energy consumption is due to the heat exchanger used to bring the CO_2 to the oxidation temperature. The main drawback of perovskites, compared to ceria, is the low re-oxidation extent unless large amounts of oxidant are used. Test 2 was performed with an excess of oxidant of 166, meaning that during the oxidation phase 166 moles of CO_2 were supplied per each mole of LSMA, and the same value was used in the simulation. An overall efficiency of 0.7% was obtained with 75% heat recuperation. However, the influence of the variation of the CO_2/LSMA ratio was not investigated, and the value of 166 may be overestimated because, in Test 2, the oxidation was performed with an equimolar mixture of N_2 and CO_2 . Therefore, further tests are needed to investigate the influence of the CO_2 flow-rate since this parameter is crucial to the overall efficiency of the process.

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