Doctoral Thesis

H₂O and CO₂ reduction by Zn and FeO for solar thermochemical fuel production

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H₂O AND CO₂ REDUCTION BY Zn AND FeO FOR SOLAR THERMOCHEMICAL FUEL PRODUCTION

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presented by
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Abstract

The thermochemical production of \( \text{H}_2 \) and \( \text{CO} \) from \( \text{H}_2\text{O}, \text{CO}_2 \) and solar energy via a two-step redox cycle is considered. The first step, driven by concentrated solar radiation, is the endothermic thermolysis of a metal oxide producing \( \text{O}_2 \) and a metal or lower valence metal oxide. The second, non-solar step is the exothermic oxidation of the metal or reduced metal oxide by \( \text{H}_2\text{O} \) and/or \( \text{CO}_2 \) to form fuel (\( \text{H}_2 \) and/or \( \text{CO} \)) and the initial metal oxide which is recycled to the solar reactor.

\( \text{Zn/ZnO} \) and \( \text{FeO/Fe}_3\text{O}_4 \) were recognized as promising redox pairs and were assessed for their ability to perform the second step of the cycle. Chemical equilibrium compositions for the systems of \( \text{Zn} \) and \( \text{FeO} \) with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) were computed as a function of temperature and pressure for different stoichiometries. A series of dynamic thermogravimetric experimental runs in the range 673-1423 K was carried out to evaluate the reaction kinetics and syngas quality of the second step. The feasibility of syngas production with both \( \text{Zn} \) and \( \text{FeO} \) was demonstrated thermodynamically and experimentally and \( \text{Zn} \) was chosen for further investigation.

The reduction of \( \text{H}_2\text{O}/\text{CO}_2 \) over mixtures of \( \text{Zn-ZnO} \) particles was investigated in a laboratory-scale packed-bed reactor as an intermediate step towards the development of the final reactor design. \( \text{ZnO} \) particles provided an effective inert support for enhancing reaction rates and final \( \text{Zn} \) conversions and enabling simple and complete recycling of solid products to the first, solar step. Experimentation was performed for solid sample compositions in the range of 33–67 wt% \( \text{ZnO} \) and inlet gas concentrations in the range 0–75% \( \text{H}_2\text{O-CO}_2 \), yielding high molar \( \text{Zn-to-ZnO} \) conversions up to 91%. A solar \( \text{Zn} \) sample produced from the solar thermolysis of \( \text{ZnO} \) which contained 75 wt% \( \text{ZnO} \) was tested in
the same reactor setup and exhibited high reactivity and conversions up to 96%. The information acquired from these small scale experiments are to be used for the development of the final reactor design.

The need for a fundamental and systematic investigation of the effect of inert solid dilution on Zn oxidation was recognized as a prerequisite for further advancements in reactor design and optimization. In a first step, the oxidation of blends of commercially available Zn with inert ZnO or Al₂O₃ particles was tested by thermogravimetry. The setup was carefully designed to ensure the absence of heat and mass-transfer intrusion on the oxidation kinetics while using a 15% CO₂ - Ar mixture or pure CO₂ in the range of 623-673 K and ambient pressure. The effects of inert particle type, mass fraction, and blending method on the reaction kinetics were studied and the information gathered combined with findings from previous studies were used to hypothesize a simplified multi-path reaction mechanism. The results imply that a kinetic model to be used for scale-up and efficiency optimization of the Zn-ZnO thermochemical cycle should not be based on investigating surrogate materials without understanding their relevance to the material they are intended to resemble.

This work contributes to the development of sustainable, clean, and efficient energy paths and offers a promising route for the production of liquid hydrocarbon fuels from H₂O, CO₂ and solar energy.
Zusammenfassung

In dieser Arbeit untersuchen wir ein 2-schritt Verfahren zur solar-thermo-chemischen Herstellung von H₂ und CO (Syngas) aus H₂O und CO₂ mittels eines Redoxreaktionspaar. Der erste Schritt, der durch konzentrierte Sonnenstrahlung getrieben wird, ist die endothermische Thermolyse eines Metalloxids, bei der O₂, Metall und ein niedervalentes Metalloxid entstehen. Der zweite Schritt, der ohne Sonneneinstrahlung abläuft, ist die exotherme Oxidation des Metalls oder des niedervalenten Metalloxids durch H₂O und/oder CO₂. Hierbei entsteht ein Treibstoff in Form von H₂ und/oder CO sowie das ursprüngliche Metalloxid, das wieder dem Solarreaktor zurückgeführt werden kann.


In einem hierfür aufgebauten Festbettreaktor wurde die Reduktion von H₂O und CO₂ oberhalb von Zn und ZnO Partikeln untersucht. Die ZnO Partikel dienten hierbei als effektiv inertes Trägermaterial, um die Reaktionsraten und die Gesamtumwandlung von Zn zu verbessern, und
ermöglichen eine einfache Handhabung während des Recyclings im ersten, solaren Schritt des Verfahrens. Die Experimente wurden mit Zusammensetzungen der festen Probe im Bereich 33-67 % Gew. sowie der zugeführten Gasprobe mit relativen Konzentrationen von H₂O zu CO₂ im Bereich 0-75% durchgeführt und erreichten molare Umwandlungen von Zn zu ZnO von bis zu 91%. Im selben Versuchsaufbau wurde eine Zn Probe getestet, die durch solare Thermolyse von ZnO gewonnen wurde. Diese Probe enthielt 75 % Gew. ZnO und zeichnete sich durch hohe Reaktivität und eine Umwandlung von bis 96% aus.

In der Folge wurde erkannt, dass die systematische Untersuchung des Einflusses der Verdünnung durch einen inerten Feststoff bei der ZnOxidation notwendig ist, um das Reaktordesign zu optimieren. Daher wurde das Oxidationsverhalten von Mischungen aus handelsüblichen Zn mit ZnO oder Al₂O₃ Partikeln mittels Thermogravimetrie untersucht. Der Versuchsaufbau wurde so gewählt, dass Wärmeübertragung und Stoffübergang keinen Einfluss auf die Oxidationskinetik nehmen konnten, wobei eine 15% CO₂ – Ar Mischung oder pures CO₂ im Temperaturbereich 623K – 673K bei Umgebungsdruck verwendet wurden. Wir erläutern den Einfluss von inerten Partikeln, bezüglich ihrer Art, des Massenanteils und der Mischmethode und leiten daraus einen vereinfachten Mehrwege-Reaktionsmechanismus ab. Abschließend vergleichen wir die erhaltenen Resultate mit Experimenten, die mit Zn/ZnO Pulvern aus dem Solarreaktor durchgeführt wurden.

Diese Arbeit trägt zu Entwicklung von nachhaltiger, sauberer und effizienter Energieversorgung bei und zeigt aussichtsreiche Wege auf, wie H₂O, CO₂ und Solarenergie zur Herstellung Kohlenwasserstoff-basierter Treibstoffe genutzt werden können.
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## Contents

Abstract ................................................................................................... i

Zusammenfassung ................................................................................ iii

Acknowledgements ................................................................................ v

Nomenclature ........................................................................................ ix

1 Introduction .................................................................................... 1

1.1 Fuel production from H₂O/CO₂ and solar energy .............. 2

1.1.1 Solar-powered electrolysis ......................................... 2

1.1.2 Photochemical routes .................................................. 3

1.1.3 Direct thermochemical H₂O and/or CO₂ splitting ..... 4

1.1.4 Solar thermochemical cycles ...................................... 5

1.2 Thesis outline ................................................................... 16

2 Evaluation of H₂O/CO₂ reduction with Zn or FeO.............. 18

2.1 Introduction...................................................................... 18

2.2 Thermodynamic analysis ................................................. 19

2.3 Experimental analysis ...................................................... 24

2.3.1 Setup ......................................................................... 24

2.3.2 Results and discussion .............................................. 27

2.4 Summary and conclusions ............................................... 33

3 Reactor engineering aspects of H₂O/CO₂ reduction with Zn... 35

3.1 Reactor design options.......................................................... 35

3.1.1 Reactors for gas-solid reactions................................. 35

3.1.2 Reactors for fluid-fluid reactions................................. 43

3.2 Laboratory-scale experiments in a packed-bed reactor ... 44

3.2.1 Motivation ................................................................ 44

3.2.2 Setup ......................................................................... 44

3.2.3 Results and discussion .............................................. 47

3.3 Summary and conclusions ............................................... 57
4 Effect of the presence of inert diluents on Zn oxidation..............59
   4.1 Theoretical background ...................................................60
   4.1.1 Kinetics of Zn oxidation ...........................................60
   4.1.2 Presence of inert solids in gas-solid reactions ..........70
   4.2 Motivation........................................................................72
   4.3 Experimental part.............................................................73
   4.3.1 Setup .........................................................................73
   4.3.2 Results ......................................................................78
   4.3.3 Discussion .................................................................89
   4.4 Summary and Conclusions ..............................................93

5 Conclusions and outlook..............................................................95
   5.1 Conclusions......................................................................95
   5.1.1 Thermodynamic and kinetic evaluation of H₂O/CO₂ reduction with Zn or FeO.......................................................95
   5.1.2 Reactor engineering aspects of H₂O/CO₂ reduction with Zn ..................................................................................96
   5.1.3 Effect of presence of inert diluents on Zn oxidation 97
   5.2 Outlook ............................................................................98
   5.2.1 Reactor development ................................................ 98
   5.2.2 Kinetic analysis of the effect of inert diluent on Zn oxidation.................................................................................99

Appendix A. Evaluation of setups for kinetic analysis ............101

List of figures .....................................................................................112

List of tables .......................................................................................117

References...........................................................................................118

Curriculum Vitae ...............................................................................133
Nomenclature

Latin characters

\( b \)  stoichiometric factor of solid reactant
\( C \)  solar flux concentration ratio
\( d \)  diameter
\( g \)  stoichiometric factor of solid product
\( HHV \)  higher heating value
\( I \)  normal beam insolation
\( Irr_{\text{quench}} \)  irreversibility from the quench unit
\( Irr_{\text{reactor}} \)  irreversibility from the reactor
\( LHV \)  lower heating value
\( l_N \)  liter under normal conditions, 273.15 K and 1 atm
\( m \)  mass
\( M \)  molar mass
\( n \)  moles of specific component
\( \dot{n} \)  molar flow rate
\( p \)  pressure
\( Q_{\text{quench}} \)  heat rejected in quench unit
\( Q_{\text{reducer}} \)  heat released from the low temperature reactor
\( Q_{\text{reactor,net}} \)  net rate of absorbed energy in solar reactor
\( Q_{\text{reradiation}} \)  radiation heat losses in solar reactor
\( Q_{\text{solar}} \)  solar power input
\( t \)  time
\( T \)  temperature
\( T_R \)  solar reactor temperature
\( T_L \)  temperature of surroundings
\( \dot{V} \)  volumetric flow rate
**Nomenclature**

\[ \dot{V}_{\text{Ar,0}} \] \hspace{1cm} \text{volumetric flow rate of purge Ar}

\[ \dot{V}_{\text{total}} \] \hspace{1cm} \text{total volumetric flow rate not including purge Ar in configuration 3}

\[ \omega_{\text{ZnO}} \] \hspace{1cm} \text{mass fraction of ZnO in sample}

\[ W \] \hspace{1cm} \text{mass fraction of the active reactant}

\[ W_f \] \hspace{1cm} \text{ratio of active to inert solids}

\[ W_{\text{FC, ideal}} \] \hspace{1cm} \text{work output of ideal fuel cell}

\[ X \] \hspace{1cm} \text{reaction extent}

\[ \text{Zn}^* \] \hspace{1cm} \text{activated Zn on ZnO surface}

\[ Z_v \] \hspace{1cm} \text{molar volume ratio of solid product to solid reactant}

**Greek characters**

\[ \alpha \] \hspace{1cm} \text{gaseous reactant molar flow fraction}

\[ \gamma \] \hspace{1cm} \text{gaseous product molar flow fraction}

\[ \Delta G \] \hspace{1cm} \text{Gibbs free-energy change}

\[ \Delta H \] \hspace{1cm} \text{enthalpy change}

\[ \Delta m \] \hspace{1cm} \text{mass change}

\[ \Delta S \] \hspace{1cm} \text{entropy change}

\[ \varepsilon \] \hspace{1cm} \text{porosity}

\[ \eta \] \hspace{1cm} \text{efficiency}

\[ \eta_{\text{absorption}} \] \hspace{1cm} \text{solar energy absorption efficiency}

\[ \rho \] \hspace{1cm} \text{density}

\[ \sigma \] \hspace{1cm} \text{Stefan-Boltzmann constant}

**Subscripts**

\[ \text{eq} \] \hspace{1cm} \text{equilibrium}

\[ g \] \hspace{1cm} \text{gas}

\[ i \] \hspace{1cm} \text{initial}
in  inert
p  solid product
r  solid reactant
s  sample
v  vapor
vol  volume

**Abbreviations**

EV  evaporator
FC  flow controller
GC  gas chromatograph
MX  mixer
MS  mass spectrometer
TC  thermocouple
1 Introduction

In 2001, approximately 86% of the global primary energy consumption (a total of $425 \times 10^{18} \text{ J}$) was supplied by fossil fuels [1]. Fossil fuels are readily available, possess a high energy density and are easily storable and transportable [2]. However, they are finite, unevenly distributed and environmentally harmful. With an expected increase of the world energy consumption rate of 1.5% yr$^{-1}$ [3], maintenance of energy and environmental security will require the development of new renewable and low carbon footprint forms of energy.

Solar energy is by far the largest exploitable resource amongst renewable energy resources as it provides globally in 1 hr more energy than the energy consumed by humans worldwide within one year [3]. In 2001 it was reported that if only 0.1% of the earth's land surface was covered with solar collectors of a collection efficiency of about 20%, the then-annual world need in energy could be covered [4]. However three major disadvantages prevent the widespread harvesting of solar energy: It is dilute, intermittent and unequally distributed [4]. For these barriers to be overcome, an energy carrier has to be developed which would increase the energy density and enhance the storability and transportability of solar energy.

An attractive method to perform the required energy conversion and storage is in the form of chemical bonds by producing solar fuels [3]. Three promising and potentially CO$_2$-neutral routes for fuel production from solar energy H$_2$O and/or CO$_2$ are: (i) electrolysis using solar generated power, (ii) photochemical/photoelectrochemical methods and (iii) thermochemical methods (direct H$_2$O/CO$_2$ splitting and solar thermochemical cycles).
1.1 Fuel production from H$_2$O/CO$_2$ and solar energy

In this section the leading routes for fuel production from water and/or CO$_2$ splitting using solar energy are briefly presented and compared with a focus on thermochemical cycles. The solar-to-fuel energy conversion efficiency is often used as the primary indicator to compare different technologies. Several definitions can be found in literature but for this section the reported efficiencies will be based on the Lower Heating Value (LHV) of the produced fuel presented as:

$$\eta_{\text{LHV}} = \frac{-\dot{n} \cdot LHV_{\text{fuel}}}{Q_{\text{solar}}}$$  \hspace{1cm} (1.1)

where \( \dot{n} \) is the molar flow rate of fuel and \( Q_{\text{solar}} \) the incident solar irradiance. In the case of water-splitting \( LHV_{\text{fuel}} \) corresponds to the enthalpy change of the reaction \( H_2 + 0.5O_2 \rightarrow H_2O_{(g)} \) at ambient temperature and pressure. In cases where the efficiency in literature was based on the Higher Heating Value (HHV) of H$_2$ the \( \eta_{\text{LHV}} \) was calculated as:

$$\eta_{\text{LHV,H}_2} = \frac{LHV_{H_2}}{HHV_{H_2}} \cdot \eta_{\text{HHV,H}_2} = 0.846 \cdot \eta_{\text{HHV,H}_2}$$  \hspace{1cm} (1.2)

1.1.1 Solar-powered electrolysis

Hydrogen production via water electrolysis using solar generated power is the most mature of all the currently available solar-to-fuel technologies. The hydrogen production unit comprises two electrodes (anode and cathode) and an external power source. The electricity can be generated either by solar cells with efficiencies ranging between 10 and 20% or Concentrating Solar Power (CSP) technologies with efficiencies 20-40% [5]. Based on these values and electrolyzer efficiencies of 42-68%, the maximum solar-to-hydrogen efficiencies have been estimated as 13.5% and 13.5-27% respectively [5].
efficiency of the overall system is limited by the solar-to-electricity efficiency of PVs and solar thermal plants and can only be improved by advancements in these technologies. Apart from engineering maturity, the electrolytic fuel production offers flexibility as it can operate with different power sources. The fuel production can continue operation during night or bad weather conditions powered from electricity generated from stored solar thermal energy or even from the power grid to minimize the effect of unpredicted weather conditions [5].

1.1.2 Photochemical routes

In photochemistry, light quanta are absorbed causing excitations from ground electronic states to excited electronic states. The transition from the excited to the ground state can give up free energy which may be stored or used for chemical synthesis. The work that can be extracted from photon absorption is limited by the product of this change of free energy and the quantum yield for the de-excitation pathway which is coupled to work production [6].

In photoelectrochemical systems, at least one light absorbing electrode is exposed to sunlight through a window and is wired internally or externally to a counter electrode to form a closed circuit and drive electrochemical reactions to split water. The light absorbing material has a dominating role to the process performance and many studies are devoted in developing materials which are highly efficient in absorbing light while resistant to electrochemical corrosion.

Photochemical systems do not require an electrode as they do not utilize electrical potential to break chemical bonds. The photons are rather absorbed by a reagent which serves as a photon sensitizer. The photons activate electrons to a higher state which are then accumulated to another reagent (catalyst) and are used to produce H₂. The lifetime and aging of the sensitizer and the catalyst are critical points in the performance of photochemical systems [5]. In comparison to
photoelectrochemical systems, photochemical systems can offer more tunability and can be implemented in homogeneous catalytic compounds simplifying the catalyst processing.

For both systems, the lack of reliance to an external power source offers simplicity through elimination of auxiliary components and can provide hydrogen in a smaller scale in comparison to other solar technologies covering the needs of fuel station or remote geographic areas. Also, the fewer parts included are less likely to fail [7]. However, they both suffer from the need for H$_2$/O$_2$ separation, difficulties with sun tracking and, very importantly, by the narrow wavelength range of photosensitive materials. The above are reflected in the overall solar-to-hydrogen efficiencies which rarely reach 13.5% for photoelectrochemical routes and 8.5% for photochemical routes [5]. The solar-to-hydrogen efficiency of an experimentally tested photochemical pilot plant was below 1% [8].

1.1.3 Direct thermochemical H$_2$O and/or CO$_2$ splitting

Direct thermochemical H$_2$O/CO$_2$-splitting in a solar reactor is the most conceptually simple and direct approach for reducing H$_2$O/CO$_2$ to fuel as represented by the reactions:

\[
\begin{align*}
CO_2 & \rightarrow CO + 0.5O_2 \\
H_2O & \rightarrow H_2 + 0.5O_2
\end{align*}
\]

for CO$_2$ splitting and H$_2$O splitting respectively.

The reactions proceed at reasonable extents at temperatures above 2500 K at 1 bar [4] where an explosive mixture of H$_2$/CO/O$_2$ is created which requires the development of an effective high temperature gas separation technique [9]. Additional material constraints imposed at such high temperatures [10] and severe re-radiation losses which lower the efficiency [11] pushed research away from this concept.
1.1.4 Solar thermochemical cycles

The infeasibility of direct H$_2$O/CO$_2$ splitting led to the investigation of solar thermochemical cycles which allow for lower maximum reaction temperatures thus alleviating the material-related constraints and for the derivation of H$_2$ and/or CO and O$_2$ in separate steps, thereby bypassing the need for their high-temperature gas separation [12].

One major class of solar thermochemical cycles for fuel production is the one utilizing metal oxide redox reactions to split H$_2$O and/or CO$_2$ in two steps. A schematic of such a cycle for syngas (mixture of H$_2$ and CO) production using a generic metal oxide redox system M$_x$O$_y$/xMO is depicted in Figure 1.1. It is divided in a solar step where solar energy is stored chemically in an energy carrier and a non-solar step where the fuel is produced. In the solar step a metal oxide is placed in solar reactor which is directly irradiated by concentrated solar energy reaching temperatures as high as 2000 K. At these temperatures the metal oxide is reduced endothermically to a metal or lower valence metal oxide which constitutes the energy carrier. The reduction step can be written as:

$$M_xO_y \rightarrow xM + \frac{y}{2}O_2$$  \hspace{1cm} (1.5)

On the second step the reduced metal is oxidized exothermically in a lower temperature chemical reactor to produce H$_2$, CO or syngas and the initial metal oxide. The reaction can be written as:

$$xM + \beta CO_2 + (1-\beta)H_2O \rightarrow M_xO_y + \beta CO + (1-\beta)H_2$$  \hspace{1cm} (1.6)

The initial metal oxide is recovered and recycled to the solar reactor, closing the cycle and resulting to the net reaction described in equation (1.7):

$$\beta CO_2 + (1-\beta)H_2O \rightarrow \beta CO + (1-\beta)H_2 + 0.5O_2$$  \hspace{1cm} (1.7)

with $0 \leq \beta \leq 1$. If the CO$_2$ utilized has been captured from air [13-15] the resulting fuel will be CO$_2$-neutral. By combining CO$_2$ and H$_2$O splitting direct production of synthesis gas (syngas, with H$_2$ and CO as main
Introduction

constituents) can be achieved. Synthesis gas can be further processed via Fischer Tropsch [16] and create low carbon footprint liquid hydrocarbons for the transportation sector.

Figure 1.1. Scheme of two step H$_2$O/CO$_2$-splitting solar thermochemical cycle for syngas production with metal oxide redox reactions.

**Thermodynamics of solar thermochemical cycles**

In this section a second law analysis is presented which has been used to assess the maximum possible energy conversion efficiency of various CO$_2$/H$_2$O splitting solar thermochemical cycles [17-21]. A typical flow diagram used for the analysis of two-step solar thermochemical cycles is shown in Figure 1.2 comprising a solar reactor, a quenching device, a H$_2$O/CO$_2$-reducing reactor and a fuel cell. In most of the analyses the complete process is assumed to take place at constant pressure while pumping work requirements and optical losses in collecting and concentrating solar energy are not taken into account. The amount of sensible and latent heat assumed to be recovered has a dramatic effect on the overall efficiency and varies from analysis to analysis.
Figure 1.2. Typical model flow diagram of a two-step solar thermochemical cycle for CO₂ splitting applied for the second-law analysis. (taken from [17])

The solar reactor is modeled as a cavity-receiver with a small aperture to allow the entrance of the concentrated solar irradiation. The solar energy absorption efficiency of the solar cavity receiver, \( \eta_{\text{absorption}} \), expresses the capability of the reactor to absorb the incoming radiation and is defined as the net rate at which energy is being absorbed divided by the radiative power entering the aperture of the solar reactor. For a perfectly insulated blackbody cavity receiver it is given by:

\[
\eta_{\text{absorption}} = \frac{Q_{\text{reactor,net}}}{Q_{\text{solar}}} = 1 - \left( \frac{\sigma T_{R}^4}{IC} \right)
\]  

(1.8)
where $I$ is the normal beam insolation, $C$ is the mean solar flux concentration ratio and $\sigma$ is the Stefan-Boltzmann constant. The reactants enter at $T_L$ and they are heated to the reactor temperature $T_R$ where depending on the assumptions they react according to equation (1.5) to reach chemical equilibrium (e.g. [18]) or full conversions (e.g. [17]). The net power absorbed in the solar reactor equals the enthalpy change rate of the reaction:

$$Q_{\text{reactor,net}} = -\dot{n}\Delta H \bigg|_{\text{reactants at } T_L \rightarrow \text{products at } T_R}$$ (1.9)

Irreversibilities arise in the solar reactor from the non-reversible chemical reaction and the re-radiation losses to the surrounding which are given by:

$$Irr_{\text{reactor}} = -\frac{Q_{\text{solar}}}{T_R} + \frac{Q_{\text{reradiation}}}{T_L} - \dot{n}\Delta S \bigg|_{\text{reactants at } T_L \rightarrow \text{products at } T_R}$$ (1.10)

The products exit the solar reactor at $T_R$ and they are quenched to $T_L$ resulting to a power loss:

$$Q_{\text{quench}} = -\dot{n}\Delta H \bigg|_{\text{products at } T_R \rightarrow \text{reactants at } T_L}$$ (1.11)

with a resulting irreversibility:

$$Irr_{\text{quench}} = \frac{Q_{\text{quench}}}{T_L} + \dot{n}\Delta S \bigg|_{\text{products at } T_R \rightarrow \text{reactants at } T_L}$$ (1.12)

The reduced species are subsequently introduced to the H$_2$O/CO$_2$ reducer where equation (1.6) takes place exothermally resulting to a heat release:

$$Q_{\text{reducer}} = -\dot{n}\Delta H \bigg|_{\text{reactants at } T_L \rightarrow \text{products at } T_L}$$ (1.13)

which in most analyses is assumed to be rejected to the surroundings. It is assumed that the products exiting both reactors separate naturally without extra work-expenditure. The irreversibilities arising in the reducer can be calculated similarly to equation (1.10) by omitting the re-radiation losses term in cases where $T_L$ is close to the temperature of the surroundings. The resulting H$_2$/CO mixture can be combusted or used in
a fuel cell to generate electricity. In this type of analysis the latter is assumed by introducing an ideal fuel cell at the end of the process resulting to an overall process exergy efficiency:

\[
\eta_{\text{exergy}} = \frac{W_{\text{FC,ideal}}}{Q_{\text{solar}}} = \frac{-\dot{n}\Delta G}{Q_{\text{solar}}} \bigg\rvert_{\text{H}_2/\text{CO}+\text{O}_2 \text{ at } 298 \text{ K} \rightarrow \text{H}_2\text{O}/\text{CO}_2 \text{ at } 298 \text{ K}}
\] (1.14)

**Promising cycles for H\textsubscript{2}O/CO\textsubscript{2} splitting**

Several hundred thermochemical cycles exist which could theoretically carry out the H\textsubscript{2}O/CO\textsubscript{2} splitting using solar energy. Screenings of the cycles have been performed to narrow down the promising candidates to a manageable number [22-24]. The criteria applied for the screening typically included the operating temperature, the number of steps and difficult separations involved, the cost, availability, corrosiveness and toxicity of process chemicals and the technical feasibility of the cycle in a first phase and the thermodynamics and theoretical efficiencies of the cycles in a second phase. Generally, there is a compromise between the maximum operating temperature and the number of the process steps of a cycle. Two step cycles have higher operating temperatures which introduce re-radiation losses and material constraints. Multistep cycles operate at lower, more workable temperatures but can achieve lower theoretical solar-to-fuel efficiency due to irreversibilities associated with each additional step and face complications related to separation of products and transportation of reactants/products after each step [25, 26]. Another critical point is the phase of the participating chemicals and the degree of difficulty of their separation. Metal oxides can be divided to volatile if sublimation occurs during the high temperature step and non-volatile if no sublimation occurs. Generally, the first category (e.g. zinc oxide, tin oxide) demonstrates rapid reaction kinetics but requires fast quenching of gaseous products to avoid their recombination, whereas the second (e.g. iron oxide, ceria, doped ferrites) exhibits structural degradation through cycling due to sintering and slower kinetics [27].
Table 1.1 presents a selection of 10 important thermochemical cycles which have demonstrated high theoretical potential and promising experimental results. The cycles are compared for water splitting in terms of $\eta_{\text{LHV}}$ and $\eta_{\text{exergy}}$ (when available) as well as for critical advantages and drawbacks. The $\eta_{\text{exergy}}$ reported were based on analyses similar to the 2$^{\text{nd}}$ law analysis presented in the previous section and none of the calculations included heat recovery.

The zinc oxide and iron oxide cycles are considered two of the most promising cycles because of their high theoretical efficiencies and relative simplicity (only two cycle steps, small number of elements involved). The ZnO cycle falls in the category of volatile systems. Therefore, it requires fast quenching of the Zn(v)/O$_2$ mixture after the reduction to avoid recombination [28] which is perhaps the greatest challenge of this process. The thermal dissociation of ZnO has been experimentally demonstrated at 1873 – 2023 K and 1 bar in Ar atmosphere using concentrated solar energy [28-31] and a kinetic rate law was determined using a solar-driven thermogravimeter [32]. Other solar processes examined for producing Zn from ZnO are the solar thermal electrolysis [33] and the solar carbothermal reduction [34]. Regarding the non-solar step, previous research has focused primarily on the reduction of H$_2$O [21, 35-43] and of CO$_2$ with Zn [44-46] in separate reactions. Zn/ZnO cycles have demonstrated an experimental sunlight-to-fuel efficiency slightly over 3% [47]. The theoretical maximum efficiency, $\eta_{\text{exergy}}$, has been calculated as 29% for H$_2$O splitting, 39% for CO$_2$ splitting and 31.5% for syngas production with a H$_2$:CO ratio of 2 [17, 20, 21]. The penalty of the Ar/O$_2$ gas separator to regenerate the inert gas needed for the quenching was considered only in the last case.
Table 1.1. Summary of characteristics of a selection of water-splitting thermochemical cycles.

<table>
<thead>
<tr>
<th>Cycle name and reaction steps</th>
<th>$\eta_{\text{exergy}}$</th>
<th>$\eta_{\text{LHV}}$</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zinc oxide</strong></td>
<td>29% [21]</td>
<td>45% $^a$ [23]</td>
<td>High theoretical efficiency; simplicity; high fraction of liberated O$_2$ per unit weight of oxide</td>
<td>Fast quenching requirement [48]</td>
</tr>
<tr>
<td>ZnO $\rightarrow$ Zn($\gamma$) + 0.5O$_2$ at 2000-2300 K</td>
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<tr>
<td>Zn + H$_2$O($\gamma$) $\rightarrow$ ZnO + H$_2$ at 600-1200 K</td>
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<tr>
<td><strong>Iron oxide</strong></td>
<td>20.4% [18]</td>
<td>42.3% $^a$ [23]</td>
<td>High theoretical efficiency; simplicity; high fraction of liberated O$_2$ per unit weight of oxide</td>
<td>High upper T causes coagulation and sintering; quenching or atmosphere with low p$_{O_2}$ required during dissociation step [26]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ $\rightarrow$ 3FeO(l) + 0.5O$_2$ at 2000-2500 K</td>
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</tr>
<tr>
<td>3FeO + H$_2$O $\rightarrow$ Fe$_3$O$_4$ + H$_2$ at 800-1000 K</td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Nickel manganese ferrite</strong></td>
<td>-</td>
<td>For $\delta=1$ 44% $^a$ [23]</td>
<td>Low operation T; high theoretical efficiencies; can cycle between steps without undergoing phase transformations [26]</td>
<td>Low fraction of liberated O$_2$ and evolved fuel per unit weight of oxide; need for vacuum or inert gas during oxide reduction [7]</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Mn$</em>{0.5}$Fe$<em>2$O$<em>4$ $\rightarrow$ Ni$</em>{0.5}$Mn$</em>{0.5}$Fe$<em>2$O$</em>{4-\delta}$ + $\frac{\delta}{2}$O$_2$ at 1273 K</td>
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<td></td>
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<tr>
<td>Ni$<em>{0.5}$Mn$</em>{0.5}$Fe$<em>2$O$</em>{4-\delta}$ + $\frac{\delta}{2}$H$<em>2$O $\rightarrow$ Ni$</em>{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ + $\frac{\delta}{2}$H$_2$ at 1073 K</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cycle name and reaction steps</td>
<td>$\eta_{\text{exergy}}$</td>
<td>$\eta_{\text{LHV}}$</td>
<td>Advantages</td>
<td>Drawbacks</td>
</tr>
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<td>-------------------------------</td>
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</tr>
<tr>
<td><strong>Cobalt ferrite</strong></td>
<td>-</td>
<td>-</td>
<td>Moderate operation $T$; can cycle between steps without undergoing phase transformations [26]; thermal stability and cyclability experimentally demonstrated [49, 50].</td>
<td>Similar to Ni$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$; suffers from sintering but it could be tackled with ZrO$_2$ support [26].</td>
</tr>
<tr>
<td>$\text{Co}<em>3\text{Fe}</em>{3-y}\text{O}<em>4 \rightarrow \text{Co}<em>3\text{Fe}</em>{3-y}\text{O}</em>{4-\delta} + \frac{\delta}{2}\text{O}_2$ at 1673 K</td>
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<tr>
<td>$\text{Co}<em>3\text{Fe}</em>{3-y}\text{O}_{4-\delta} + \frac{\delta}{2}\text{H}_2\text{O} \rightarrow \text{Co}<em>3\text{Fe}</em>{3-y}\text{O}_4 + \frac{\delta}{2}\text{H}_2$ at 1073 K</td>
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<tr>
<td><strong>Nickel ferrite</strong></td>
<td>-</td>
<td>-</td>
<td>Similar to cobalt ferrites; thermodynamic calculations suggest it has the best combination of properties for solar H$_2$O spitting relative to other ferrites [51].</td>
<td>Similar challenges to cobalt ferrites.</td>
</tr>
<tr>
<td>$\text{Ni}<em>3\text{Fe}</em>{3-y}\text{O}<em>4 \rightarrow \text{Ni}<em>3\text{Fe}</em>{3-y}\text{O}</em>{4-\delta} + \frac{\delta}{2}\text{O}_2$ at 1673 K</td>
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<tr>
<td>$\text{Ni}<em>3\text{Fe}</em>{3-y}\text{O}_{4-\delta} + \frac{\delta}{2}\text{H}_2\text{O} \rightarrow \text{Ni}<em>3\text{Fe}</em>{3-y}\text{O}_4 + \frac{\delta}{2}\text{H}_2$ at 1073 K</td>
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<tr>
<td><strong>Cerium oxide</strong></td>
<td>-</td>
<td>-</td>
<td>Moderate maximum $T$; no phase change of oxide; rapid fuel production; higher stability and selectivity than ferrites [53].</td>
<td>Lower liberated O$_2$ per unit weight of oxide than ferrites [47].</td>
</tr>
<tr>
<td>$\text{CeO}<em>2 \rightarrow \text{CeO}</em>{2-\delta} + \frac{\delta}{2}\text{O}_2$ at 1700-1900 K</td>
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<tr>
<td>$\text{CeO}_{2-\delta} + \delta\text{H}_2\text{O} \rightarrow \text{CeO}_2 + \delta\text{H}_2$ at 1000-1273 K</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tin oxide</strong></td>
<td>29.8% [19]</td>
<td>30.4% $^b$ [19]</td>
<td>Similar to ZnO cycle; possibly lower reduction $T$ for SnO$_2$ than ZnO; dissociation rate of SnO$_2$ possibly less dependent on quenching rate than ZnO [19].</td>
<td>Similar to those of ZnO; slower reaction rate in hydrolysis step than Zn [54].</td>
</tr>
<tr>
<td>$\text{SnO}<em>2 \rightarrow \text{SnO}</em>{(g)} + 0.5\text{O}_2$ at 1873 K</td>
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<tr>
<td>$\text{SnO} + \text{H}_2\text{O} \rightarrow \text{SnO}_2 + \text{H}_2$ at 823 K</td>
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<td></td>
</tr>
<tr>
<td>Cycle name and reaction steps</td>
<td>$\eta_{\text{exergy}}$</td>
<td>$\eta_{\text{LHV}}$</td>
<td>Advantages</td>
<td>Drawbacks</td>
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</tr>
</tbody>
</table>
| Sodium manganese-3           | 42% or 20% with product separation [55] | 50% [23] | Moderate operating temperatures; potentially straightforward MnO/O
2 separation [25]; Mn2O3 reduction thermodynamically favored in air [56]. | 3 steps; NaOH/ Mn2O3 separation; corrosiveness of NaOH; multiple oxide species separation [26, 55-57]. |
| Sulfur-iodine (GA)           | 29.6% [58] | 38.1% a [23] | Low operating temperatures; extensively investigated for nuclear heat sources [24]. | 3 steps; costly separations of chemicals [25, 59]; unwanted side reactions; involves corrosive chemicals [25]. |
| Calcium iron Bromide-2 (UT-3)| 33.8% a [23] | Low operating temperatures; extensively investigated for nuclear heat sources [24]. | Four steps; involves corrosive/toxic chemicals; HBr/ H2 separation necessary [26]; high steam mass flows required [23]. |

a Accounts for shaft and pumping work; assumes 50% electricity generation efficiency; not clear if $\eta_{\text{absorption}}$ is accounted for.

b $\eta_{\text{absorption}}$ is taken into account; shaft and pumping work neglected.
The iron oxide cycle falls in the category of non-volatile oxides. The thermal dissociation of Fe$_3$O$_4$ to FeO has been experimentally demonstrated at temperatures between 1673 – 2273 K and pressures 0.1-1 bar in both inert and air atmospheres using solar furnaces [60-62]. Low oxygen partial pressures are needed to achieve reduction of Fe$_3$O$_4$ [26]. The non-solar step has been demonstrated both for H$_2$O reduction [37, 61, 63] and CO$_2$ reduction [44, 64-70] in separate reactions. The theoretical maximum efficiencies, $\eta_{exergy}$, of the FeO/Fe$_3$O$_4$ H$_2$O-splitting and CO$_2$-splitting cycles have been calculated as 20.4% and 29% respectively [17, 18]. A critical issue with this cycle is the deactivation of the oxide during the high temperature step. The reduction takes place above the FeO melting point resulting to a sintered, non-porous product and milling is essential to re-activate the oxide. Partial substitution of the Fe in the magnetite phase by a metal cation results in formation of mixed ferrites of the type M$_x$Fe$_{3-x}$O$_4$ (M = Co, Ni, Zn, Mg) which are expected to have more moderate thermal reduction temperatures and avoid the FeO fusion. Several mixed ferrites were experimentally investigated [63, 71-73] but none was able to demonstrate high activity and good repeatability. Supporting the ferrites on zirconia was shown to alleviate the problems caused by sintering and increase the activity and cyclability [74, 75]. Recently, NiFe$_2$O$_3$ and CoFe$_2$O$_3$ were identified as the most promising amongst several spinel redox pair materials tested in a packed bed reactor as they demonstrated thermal stability and good cyclability between the reduction/oxidation steps [76]. The main drawbacks of the mixed ferrites are the need for low oxygen partial pressures in the high temperature step and the low fraction of oxygen evolved and H$_2$/CO produced relative to the weight of the solid reactant which makes heat recovery essential for the viability of the cycles. Previous research on the non-solar step has focused on the reduction of H$_2$O with FeO/ferrites [37, 61, 63, 77-81] and of CO$_2$ with FeO/ferrites [44, 46, 64-70, 82-87] in separate reactions. Concurrent splitting of H$_2$O and CO$_2$ with Fe-based metals has also been considered [88] and a synergistic effect in the competitive
reaction mechanism that leads to higher product yields was reported for ferrites [89].

Cerium oxides have emerged as promising redox materials as they have exhibited fast kinetics relative to other non-volatile systems like mixed ferrites [90-92]. The reduction of CeO\textsubscript{2} to Ce\textsubscript{2}O\textsubscript{3} which occurs above 2273 K causes fusion and vaporization of the material [93] but partial, non-stoichiometric reduction can occur at more moderate temperatures and was proven stable for 500 cycles [91]. However, similarly to non-stoichiometric ferrites, the cerium oxide cycle suffers from a low O\textsubscript{2} release relative to the total oxide mass. A thermodynamic analysis revealed the potential of raising the relatively low $\eta_{LHV} = 17\%$ to $\eta_{LHV} = 25\%$ by recovering the sensible heat of the products [52]. Separate and concurrent splitting of H\textsubscript{2}O and CO\textsubscript{2} with Ce-based metals has been demonstrated [53, 94] and a peak experimental $\eta_{LHV} = 3.53\%$ was measured accounting also for the penalty induced by the inert gas usage [95]. The performance was dramatically improved by substituting the optically thick ceria previously contained in the solar reactor by a reticulated porous ceramic foam made of pure CeO\textsubscript{2} [95].

The tin oxide cycle is also a volatile system and has similar advantages and challenges to the zinc oxide cycle. Both stages of the cycle have been experimentally investigated [19, 54, 96] and the results indicate that the tin oxide reduction can proceed at lower temperatures than the ZnO reduction resulting to slightly higher $\eta_{exergy}$ [19]. The reduction efficiency of SnO\textsubscript{2} was shown to be less dependent on the quenching rate than that of ZnO [19] but SnO hydrolysis was shown to proceed with lower reaction rates than Zn hydrolysis [54].

The sodium manganese-3 cycle has good potential because of the high theoretical efficiencies, moderate temperatures, seemingly straightforward MnO/ O\textsubscript{2} separation during the high temperature step and possibility of reduction in air. Drawbacks include the challenging Mn\textsubscript{2}O\textsubscript{3}/NaOH separation, the corrosive nature of NaOH and the multiple oxides produced which can complicate the separations [55, 56].
Finally, the GA and UT-3 cycles have been mainly investigated for using a nuclear heat source [59, 97] and are considered the most promising low temperature cycles [24]. Their low maximum operation temperature is an intriguing advantage but they both include corrosive chemicals and multiple reactions which introduce several complications mainly in separation of reactants/products. The high gas mass flows, need for membrane development and limited possibilities for efficiency improvements have moved research away from the UT-3 cycle whereas the GA cycle is still considered a promising candidate [23, 26].

Overall, the experimentally demonstrated efficiencies are currently much higher for solar-powered electrolysis, but fuel production using solar thermochemical cycles has the potential of becoming more efficient and therefore more cost-effective. Photochemical and photoelectrochemical routes also have high theoretical efficiencies but are limited by the wavelength range of photoelectrodes and photocatalysts and have a long journey ahead on their way to commercialization.

1.2 Thesis outline

The project aimed at the development of a sustainable and clean fuel production method using \( \text{H}_2\text{O}, \text{CO}_2 \) and sunlight by investigating two-step solar-thermochemical cycles to efficiently reduce \( \text{CO}_2 \) and/or \( \text{H}_2\text{O} \) using redox reactions (e.g. \( \text{Zn}/\text{ZnO}, \text{FeO}/\text{Fe}_3\text{O}_4 \)). The focus of the research is the fabrication of a reactor to perform the second step of the cycle. Literature research, chemical thermodynamics and kinetic studies were employed to provide the fundamental knowledge needed for an effective reactor to be designed and fabricated.

In Chapter 2, \( \text{Zn}/\text{ZnO} \) and \( \text{FeO}/\text{Fe}_3\text{O}_4 \) redox pairs are chosen as promising candidates to carry out the concurrent \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) splitting via solar thermochemical cycling. A thermodynamic analysis and a kinetic study via dynamic thermogravimetric experiments are performed.
as an assessment of the potential of the two redox pairs with a focus on the second step of the cycle.

In Chapter 3, the kinetic investigation of the reduction of H₂O/CO₂ over Zn-ZnO blends in a packed bed reactor is presented as an intermediate step towards the development of the final reactor design. The effects of initial sample mass, ZnO mass fraction and gaseous oxidant composition on the reaction rate and final conversion are evaluated.

In Chapter 4, a more fundamental and systematic investigation of the effect of inert solid dilution on Zn oxidation is recognized as a prerequisite for further advancements in reactor design and optimization. The effects of inert particle type, mass fraction, and blending method on the reaction rate and asymptotic conversion are studied in a thermogravimetric balance which is evaluated for heat and mass transfer intrusion as shown in Appendix A. The results combined with previous literature findings are used to propose a simplified multi-path reaction mechanism.

Chapter 5 summarizes the important findings and main conclusions of this thesis. Suggestions for future work are provided.

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2 Evaluation of H$_2$O/CO$_2$ reduction with Zn or FeO$^1$

Two-step solar thermochemical cycles based on Zn/ZnO and FeO/Fe$_3$O$_4$ redox reactions are proposed for producing synthesis gas from H$_2$O and CO$_2$ as sole chemical sources. A thermodynamic analysis is performed to determine the equilibrium composition and energy requirements of the H$_2$O/CO$_2$ reduction step over a selected range of temperatures, pressures, and stoichiometries, and to guide the operating conditions for the experimental studies. An experimental thermogravimetric analysis is carried out to for a first assessment of the reaction kinetics and produced syngas quality potential of the two candidates.

2.1 Introduction

As demonstrated Chapter 1, Zn/ZnO and FeO/Fe$_3$O$_4$ redox pairs are promising candidates for CO$_2$ and/or H$_2$O splitting via solar thermochemical cycling [22, 27, 98].

The reduction steps can be represented as:

\[ ZnO \rightarrow Zn + 0.5O_2 \quad \Delta H_{298K}^\circ = 350.5 \text{ kJ mol}^{-1} \quad (2.1) \]

\[ Fe_3O_4 \rightarrow 3FeO + 0.5O_2 \quad \Delta H_{298K}^\circ = 316.6 \text{ kJ mol}^{-1} \quad (2.2) \]

and the oxidation reactions can be represented as:

---

\[ Zn + \beta CO_2 + (1 - \beta)H_2O(v) \rightarrow ZnO + \beta CO + (1 - \beta)H_2 \] (2.3)

\[ -108.8 \text{ kJ mol}^{-1} < \Delta H_{298K}^\circ < -67.5 \text{ kJ mol}^{-1} \]

\[ 3FeO + \beta CO_2 + (1 - \beta)H_2O(v) \rightarrow Fe_3O_4 + \beta CO + (1 - \beta)H_2 \] (2.4)

\[ -77.8 \text{ kJ mol}^{-1} < \Delta H_{298K}^\circ < -33.6 \text{ kJ mol}^{-1} \]

Previous research has focused primarily on the reduction of H₂O with Zn [21, 35-37] and FeO/ferrites [37, 61, 63, 77-81] and of CO₂ with Zn [44-46] and FeO/ferrites [44, 46, 64-70, 82-87] in separate reactions. This study considers the simultaneous reduction of H₂O and CO₂. Zn reactions with mixtures of H₂O/CO₂/H₂/CO have been investigated within the framework of the Imperial Smelting Process [99].

### 2.2 Thermodynamic analysis

Thermodynamic equilibrium computations were carried out for the Zn/CO₂/H₂O and FeO/CO₂/H₂O systems, using the minimization of the free Gibbs energy function [100]. Species with mole fractions of less than 10⁻⁵ were omitted from the figures. Figure 2.1 and Figure 2.2 show the variation of the equilibrium compositions of the gas and solid phases, respectively, as a function of temperature at 1 bar for both Zn and FeO systems, and at different stoichiometries: 2Zn+H₂O+CO₂ (Figure 2.1a and Figure 2.2a), 3Zn+H₂O+CO₂ (Figure 2.1b and Figure 2.2b), 6FeO+H₂O+CO₂ (Figure 2.1c and Figure 2.2c), and 9FeO+H₂O+CO₂ (Figure 2.1d and Figure 2.2d). The initial Zn or FeO to H₂O/CO₂ molar ratios were chosen to favor CO/H₂ or C/CH₄ production.

For both Zn containing reactions, C and CH₄ production is favored at lower temperatures and at higher initial Zn, although C is unlikely to be formed [44]. For the 2Zn+H₂O+CO₂ system, the formation of H₂ and CO is favored at intermediate and high temperatures, respectively. H₂ formation begins at above 500 K and peaks at about 1100 K, while CO formation begins at above 750 K and peaks at about 1250 K. Production
of syngas with H₂:CO ratio of ~2 is then thermodynamically favorable in the range 950 – 1050 K. The equilibrium behavior is analogous for the 3Zn+H₂O+CO₂ system, except that a significant amount of CH₄ is observed at low temperatures. CO production is shifted to the right due to favored C production over a wider temperature range of 500-1200 K and coincides with high quality syngas being shifted to higher temperatures. For both stoichiometries, complete conversion of Zn-to-ZnO is observed below 1000 K as seen in Figure 2.2. Above 1000 K, the endothermic carbothermal reduction of ZnO becomes possible and Zn(g) is present in equilibrium.

![Diagram](image-url)  
**Figure 2.1.** Equilibrium composition of the gaseous products and solid carbon versus temperature at 1 bar for the systems: a) 2Zn+H₂O+CO₂, b) 3Zn + H₂O+CO₂, c) 6FeO+H₂O+CO₂, and d) 9FeO+H₂O+CO₂.
For the $6\text{FeO} + \text{H}_2\text{O} + \text{CO}_2$ system, C formation is thermodynamically favorable over the temperature range 400-800 K. Small amounts of CH$_4$ are formed up to 700 K. H$_2$ appears at above 500 K and peaks at 900 K, while CO formation starts at above 800 K and becomes increasingly favorable above 1150 K. Production of syngas is then thermodynamically favorable at ~900K.

Between 400-500 K, the majority of the FeO is converted to Fe$_3$O$_4$ with residuals amounts of Fe$_2$O$_3$. Above 500 K, non-stoichiometric wustite increases monotonically with temperature. From 800-1000 K, a
small amount of FeO is reduced to Fe. For the $9\text{FeO} + \text{H}_2\text{O} + \text{CO}_2$ system, the equilibrium composition is different at low temperatures. Between 400-450 K, there is an equimolar formation of CH$_4$ and C. Above 450 K, CH$_4$ decreases while C increases and peaks at 750 K. The H$_2$, CO, and Fe containing products follow the same trend as the $6\text{FeO} + \text{H}_2\text{O} + \text{CO}_2$ system.

The enthalpy change of the pertinent reactions as a function of temperature is shown in Figure 2.3, with reactants at 298 K and products at equilibrium at the corresponding temperature.

![Figure 2.3. Enthalpy change of the reactions as a function of temperature for the chemical systems: a) $2\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ and $3\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ and b) $6\text{FeO}+\text{H}_2\text{O}+\text{CO}_2$ and $9\text{FeO}+\text{H}_2\text{O}+\text{CO}_2$ assuming reactants at 298 K and products at equilibrium at the given temperature.](image)

The $\Delta H$ of both systems increases with temperature mainly because of the increasing sensible heat absorbed. The $3\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ reaction is more exothermal than the $2\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ at lower temperatures due to the high exothermicity of C and CH$_4$ formation. The change in the slope for the $3\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ after 1000 K corresponds to lower conversions of CO$_2$ and H$_2$O to CH$_4$ and C. The change of slope at same temperatures for $2\text{Zn}+\text{H}_2\text{O}+\text{CO}_2$ system is also attributed to the decrease of C. Both systems turn endothermic at 1250 K. For the
FeO/H₂O/CO₂ reactions, 9FeO+H₂O+CO₂ system is more exothermic than the 6FeO+H₂O+CO₂ system below 720 K, primarily because of higher CH₄ formation. The high C formation also has a significant role, especially at the range of 600-800K. Both reactions turn endothermic at 720 K and above this point the system 6FeO+H₂O+CO₂ becomes the least endothermic.

The reaction extents $X$ are defined for the 2Zn+H₂O + CO₂ and 6FeO+H₂O+CO₂ systems with respect to C, CO, and H₂ in equations (2.5), (2.6), (2.7), respectively, as:

$$X_C = \frac{2n_{C}^{eq}}{n_{Zn}^{in}} \quad \text{or} \quad \frac{6n_{C}^{eq}}{n_{Feo}^{in}}$$

(2.5)

$$X_{CO} = \frac{n_{CO}^{eq}}{n_{Zn}^{in}} \quad \text{or} \quad \frac{3n_{CO}^{eq}}{n_{FeO}^{in}}$$

(2.6)

$$X_{H_2} = \frac{n_{H_2}^{eq}}{n_{Zn}^{in}} \quad \text{or} \quad \frac{3n_{H_2}^{eq}}{n_{FeO}^{in}}$$

(2.7)

where $n_{in}^{in}$ and $n_{eq}^{eq}$ denote the initial and equilibrium amount, respectively. $X_C$, $X_{CO}$, and $X_{H_2}$ as a function of temperature for pressures between 0.1-10 bars are given in Figure 2.4a, b for the 2Zn+H₂O+CO₂ system and in Figure 2.4c, d for the 6FeO+H₂O+CO₂ system. Figure 2.4a, c shows the $X$ of the main products which contain C while Figure 2.4b, d shows the syngas components. For both Zn and FeO system, higher pressures favor the production of C over CO, which is consistent with Le Chatelier’s principle. Therefore, the production of syngas is shifted to higher temperatures with increasing pressure. $X_{H_2}$ and $X_{CO}$ reach much higher values in the Zn system than in the FeO system, which translates to higher syngas production. For the Zn system at 1 bar, the peak values of $X_{H_2}$ and $X_{CO}$ are around 0.4 whereas for the FeO system they are less than 0.15.
2.3 Experimental analysis

2.3.1 Setup

FeO and Zn were reacted with different concentrations of CO\textsubscript{2} and H\textsubscript{2}O in the thermogravimetric experimental setup (TG, Netzsch 409STA), schematically shown in Figure 2.5. Initially, 100 mg samples of Zn (Sigma-Aldrich, 98+%) and FeO (Sigma-Aldrich, 99+%) were placed on an Al\textsubscript{2}O\textsubscript{3} crucible supported by an alumina rod that
incorporated a thermocouple. Additional information about the Zn and FeO powders are listed in Table 2.1. The chamber was vacuumed and subsequently flashed with Argon (PanGas, purity 99.999 %). This procedure was repeated three times to ensure that the level of O₂ was below 300 ppm. The chamber was heated in Ar at a rate of 10 K/min to the desired temperature. Once the temperature was stabilized, the gaseous reactants were introduced into the lower part of the TG, flowed along the walls, and entered the chamber from the top. The gaseous reactants into the system consisted of different mixtures of CO₂ (Pangas 4.5, ≥ 99.995%), and H₂O (generated from a Bronkhorst steam generator). The total flow rate of H₂O and CO₂ was fixed at 100 mlN/min². All experiments were performed at ambient pressure. The product gases exiting from the bottom of the chamber were cooled to condense out the H₂O and finally analyzed by gas chromatography (GC, Varian cp4900 equipped with Molsieve-5A/Poraplot-U columns). Blank runs were performed to account for the effects of buoyancy and thermal expansion of gases on the TG measurements.

A series of dynamic experiments was performed to evaluate the competitive nature of the reaction resulting in syngas production. The temperatures for reactions (2.3) and (2.4) were increased from 673 - 1173 K and 923-1423 K, respectively. The molar flow fractions of gaseous reactants, \( \alpha \), and products, \( \gamma \), are defined in eqs.(2.8) and (2.9), respectively, as:

\[
\alpha = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO_2} + \dot{n}_{H_2O}} \quad (2.8)
\]

\[
\gamma = \frac{\dot{n}_{CO}}{\dot{n}_{CO} + \dot{n}_{H_2}} \quad (2.9)
\]

\(^2\) lN designates liter under normal conditions, 273.15 K and 1 atm
where $\dot{n}$ denotes molar flow rate. For both reactions, the heating rate was 10 K/min, and $\alpha$ was varied from 0.2 - 0.9.

Figure 2.5. Thermogravimetric experimental setup.

The reaction extents, $X_{Zn}$ and $X_{FeO}$, were calculated using the TG mass gains and are given in eqs. (2.10) and (2.11), respectively, as:

$$X_{Zn} = \frac{\Delta m M_{Zn}}{(M_{ZnO} - M_{Zn})m_i}$$  \hspace{1cm} (2.10)

$$X_{FeO} = \frac{3\Delta m M_{FeO}}{(M_{Fe_2O_4} - 3M_{FeO})m_i}$$  \hspace{1cm} (2.11)

where $\Delta m$ denotes the mass change, $m_i$ the initial sample mass, and $M$ the molecular weight.
Table 2.1. Properties of Zn and FeO powders used in the TG experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>d_{\text{mean}}, \mu m</th>
<th>S_{\text{BET}}, m^2/g</th>
<th>Impurities</th>
<th>Titration</th>
</tr>
</thead>
</table>
| Zn       | 6.7                      | 5.00                   | As: \leq 0.1 mg/kg  
            |                           |            | Cd: \leq 500 mg/kg  
            |                           |            | Cu: \leq 50 mg/kg      
            |                           |            | Fe: \leq 50 mg/kg      
            |                           |            | Pb: \leq 500 mg/kg     
            |                           |            | Sn: \leq 10 mg/kg      |
| FeO      | 400-630                 | 6.12                   | \leq 5% free iron 99.9% 
            |                           |            | Pure (based on TMI)    
            |                           |            | <1000 ppm total metallic impurities (based on emission spectra) |

2.3.2 Results and discussion

$X_{\text{Zn}}$ and $X_{\text{FeO}}$ as a function of $t$ and $T$ are shown in Figure 2.6 for various values of $\alpha$. 
Figure 2.6. Reaction extents (solid lines) and temperature (dashed lines) versus time for dynamic TG runs performed with a) CO₂-H₂O/Zn and b) CO₂-H₂O/FeO at various gaseous reactant concentrations.

The reaction for the CO₂-H₂O/Zn system began at about 750 K and peaked at 850-1000 K for all runs. The reaction rates decreased significantly when $X_{Zn} > 0.85$, which has been previously attributed to a transition from an interface-controlled regime to a diffusion-controlled regime[44]. For all experiments, $X_{Zn}$ reached 0.85-0.95 after 45 min. The reaction for the CO₂-H₂O/FeO system commenced immediately after the reactive gas was introduced into the system. Initially, high reaction rates
were observed over the first 5 min of the experiment, indicating rapid oxidation of the particle surface. Afterwards, they remained relatively constant before transitioning to the diffusion-controlled regime after 45 min. For all experiments, $X_{FeO} > 0.8$ after 50 min. of reaction. For both systems, no direct correlations were identified between $\alpha$ and reaction rates.

Figure 2.7 a,b show the product gas composition during exemplary dynamic runs for the CO$_2$-H$_2$O with Zn and FeO, respectively. $X_{Zn}, X_{FeO}, \dot{n}_{H_2}, \text{ and } \dot{n}_{CO}$ are given as functions of $t$ and $T$ at $\alpha=0.5$. The non-linear shape of the Zn and FeO conversion curves indicates that the measurements are free of mass transfer limitations from the bulk flow to the external surface of the sample which is often an issue in thermogravimetric setups (see Appendix A). For CO$_2$-H$_2$O/Zn system, the production of CO and H$_2$ started at about 780 K. The molar flow rate of H$_2$ peaked at 1000 K whereas the one for CO peaked at 1060 K, which is consistent with the thermodynamic calculations favoring CO over H$_2$ at higher temperature. The amount of H$_2$ produced was much higher than the corresponding CO, indicating a kinetically favored reaction of Zn with H$_2$O rather than with CO$_2$. The profile of gas production is remarkably different for CO$_2$-H$_2$O/FeO system, which took place at higher $T$. A high peak of H$_2$ was observed at the beginning of the reaction which corresponded to the initial fast mass gain measured by the TG. This peak indicated a preferential reaction of H$_2$O with the FeO particles. After 1000 K, H$_2$ production stabilized and remained constant until 1300 K where it decreased. The CO production reached its highest value at 950 K and remained almost constant until 1300 K when it started to decrease. It should be noted that other intermediate reactions might also take place at the systems examined. More specifically, the water-gas shift reaction (WGSR) may occur, altering the composition of the product gases as they travel downstream to the GC. The thermodynamics predict that below 1100 K the WGSR takes place, shifting the equilibrium towards H$_2$ production, whereas
above 1100 K the reverse WGSR is thermodynamically favored, shifting the equilibrium towards CO production.

Figure 2.7. Reaction extents (solid lines) and molar flow rates of CO (squares) and H₂ (circles) versus time and temperature for: a) CO₂-H₂O/Zn system; and b) CO₂-H₂O/FeO system. The molar flow fractions of the gas is α = 0.5.
Although thermodynamically favorable, no C or CH₄ formation was observed throughout the experiments, as verified by GC and mass balances. \( X_{Zn} \) and \( X_{FeO} \) and the normalized amounts of accumulated H₂, CO and \( H_2+CO \) are given for CO₂-H₂O/Zn and CO₂-H₂O/FeO systems in Figure 2.8 a and b, respectively, as a function of \( t \) with \( \alpha = 0.2 \). The normalized amounts of accumulated \( H_2+CO \) from the GC predict slightly lower reaction extents compared with the \( X_{Zn} \) and higher reaction extents compared with \( X_{FeO} \). For the CO₂-H₂O/FeO system, the CO and H₂ concentrations were below the detection limit in the diffusion-controlled regimes. The solid products were only ZnO and Fe₃O₄, as verified by X-ray diffraction analysis. This can be attributed to kinetic hindrances as well as to the fact that, through the continuous feeding of reactive gas and removal of the gaseous products, the experimentally investigated system was not allowed to reach thermodynamic equilibrium.

In both systems, the resulting H₂:CO ratio exhibited a strong dependency on \( \alpha \), which can be seen in Figure 2.9. Integrated values of \( \gamma \) over time were used to compare the experiments. Both Zn and FeO are able to produce syngas with H₂/CO molar ratios in ranges between 1.7-2 (corresponding to \( \gamma = 0.37-0.33 \) ) which can be readily converted to liquid hydrocarbons via Fischer-Tropsch without further adjustment of the syngas composition. A linear dependency between \( \gamma \) and \( \alpha \) for both reactions was observed. These correlations reveal the possibility of adjusting the syngas composition by varying the reactant flows.
Figure 2.8. Reaction extents (solid lines) and the accumulated normalized amounts of CO (squares), H₂ (circles), and H₂+CO (diamonds) versus time for: a) CO₂-H₂O/Zn system; and b) CO₂-H₂O/FeO system. The molar flow fractions of the gas is $\alpha = 0.2$. 
2.4 Summary and conclusions

Two-step solar thermochemical cycles were examined to reduce simultaneously CO$_2$ and H$_2$O to syngas using Zn/ZnO and FeO/Fe$_3$O$_4$ redox pairs. The feasibility of syngas production with both Zn and FeO was proven both thermodynamically and experimentally. Thermodynamic equilibrium computations revealed that the formation of C is favored at temperatures below 1000 K and that high quality syngas can be produced for both systems at temperatures above 900 K. The two reactions were also investigated in dynamic thermogravimetric experiments combined with gas chromatography in the temperature range of 673 - 1173 K for Zn and 923-1423 K for FeO. For the largest part of the reactions of both Zn and FeO, H$_2$O exhibited higher reaction rates with the solids compared to CO$_2$. A strong dependency between the H$_2$O/CO$_2$ molar ratio of the input gases and the H$_2$/CO molar ratio of
the product gases was shown which in an industrial application could be used to adjust the produced syngas to the composition readily suitable for further processing. Contrary to the thermodynamic calculations, no methane or carbon production was observed and only ZnO and Fe$_3$O$_4$ were attained as solid products. The discrepancies between the thermodynamic predictions and the experimental results can be attributed to kinetic hindrances as well as to the fact that, through the continuous feeding of reactive gas and removal of the gaseous products, the experimentally investigated system was not allowed to reach thermodynamic equilibrium. Both solid reactants exhibited similar conversion rates and final reaction extents. However, Zn reacted at a lower temperature range and, as shown in Chapter 1, has a higher maximum theoretical solar-to-fuel efficiency and is thereby chosen for further investigation.
3 Reactor engineering aspects of H₂O/CO₂ reduction with Zn³

The feasibility of concurrent H₂O and CO₂ splitting for syngas production has been thermodynamically and experimentally demonstrated for Zn and FeO in Chapter 2 and Zn was chosen for further investigation. In this chapter, a packed-bed reactor is fabricated to test concurrent CO₂ and H₂O reduction for the direct syngas production over Zn particles in a larger scale.

3.1 Reactor design options

3.1.1 Reactors for gas-solid reactions

Five reactor types commonly used to carry out gas-solid reactions are considered as candidates for the Zn oxidation reactions. Simple schematics of the reactors are shown in Figure 3.1. The most basic type is the packed bed reactor where the gaseous reactants are flowing through a cylindrical tube which is filled with solid particles (Figure 3.1a). The moving bed reactor (Figure 3.1b) is similar to the packed bed but the particles are continuously fed to the top of the bed under the influence of gravity and are removed from the bottom of the reactor. In a fluidized bed (Figure 3.1c), the gaseous reactants flow at rates that are sufficiently high to lift the particles and create a suspension of

³ Material from this chapter has been published in: Stamatiou A, Loutzenhiser PG, Steinfeld A. Syngas production from H₂O and CO₂ over Zn particles in a packed-bed reactor. AIChE J. 2012;58:625-3.
continuously moving solids but not high enough to carry them out of the reactor. In the pneumatic conveying reactor the particles are widely dispersed in the gas phase and both solid and gas phases are continuously flowing through the reactor (Figure 3.1d). Finally, in a rotary cylinder reactor the solids are contained in a rotating tilted cylinder and are flowing in one direction while coming in contact with a gaseous reactant flow which is typically fed in the opposite direction (Figure 3.1e). Table 3.1, presents a summary of several key characteristics of these five reactor types found in [101-103].
Figure 3.1. Common reactor types used for gas-solid reactions.
Table 3.1. Comparison of main gas-solid reactor types (based on tables found in [101, 102] with additional information found in [103])

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Particle size</th>
<th>Solid flow</th>
<th>Gas flow</th>
<th>Pressure drop</th>
<th>Agglomeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed</td>
<td>Large/uniform (typically 0.6 - 300 mm)</td>
<td>No solid flow.</td>
<td>Near plug flow, upwards or downwards.</td>
<td>High for fine particles, low for large particles.</td>
<td>Can be significant.</td>
</tr>
<tr>
<td>Fluidized bed</td>
<td>Smaller particles (typically 0.01 - 3 mm)</td>
<td>Near perfect mixing.</td>
<td>Complex flow, inefficient contacting, bypassing.</td>
<td>High for deep beds.</td>
<td>Can be significant.</td>
</tr>
<tr>
<td>Pneumatic conveying</td>
<td>Fine particles (typically 0.02 - 0.08 mm)</td>
<td>Near plug flow, problems with solid distribution, recirculation of fines is crucial.</td>
<td>Near plug flow.</td>
<td>Low for fine particles, high for larger particles.</td>
<td>No problem.</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Temperature gradients</td>
<td>Heat exchange/heat transport</td>
<td>Other characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------</td>
<td>-------------------------------</td>
<td>------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed bed</td>
<td>Large especially in highly exothermic/endothermic reactions.</td>
<td>Inefficient exchange, large heat exchanger surface required.</td>
<td>Simple, low cost solution for semi-batch operation. Inefficient particle loading/unloading. 100% theoretical conversion possible.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moving bed</td>
<td>Large but can be controlled by gas flow and solid circulation.</td>
<td>Inefficient exchange but heat transport by particle circulation possible.</td>
<td>100% theoretical conversion possible.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidized bed</td>
<td>Small, near isothermal operation can be achieved.</td>
<td>Efficient heat exchange and energy transport by particle circulation.</td>
<td>For high conversion special design is necessary (e.g. staging, multiple beds, gas recycling).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pneumatic conveying</td>
<td>Significant but can be minimized by solid circulations.</td>
<td>Intermediate between packed and fluidized bed.</td>
<td>Only suitable for very fast reactions. Fast intraparticle heat and mass transfer possible due to small particle size. High excess gas requirement to entrain particles.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotary cylinder</td>
<td>Severe gradients may arise in the solid flow direction.</td>
<td>Poor exchange, long cylinders required.</td>
<td>High theoretical conversions possible as a result of countercurrent plug flow.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The concept could be modified for direct dispersion of Zn particles coming out of the solar reactor without evaporation and condensation thus avoiding the deposition on the walls and the energy penalty associated with Zn evaporation. However, oxidation of commercial Zn particles with different morphologies but similar or smaller particle size to the particles produced in solar reactor indicated that the reaction time needed for reasonable Zn-to-ZnO conversions will be in the order of minutes [36] and therefore the residence times achievable in a pneumatic transport reactor are too low for this process.

Figure 3.2. Representative scheme of aerosol flow reactor for $\text{H}_2\text{O}$ or $\text{CO}_2$ splitting with Zn (based on [45]).
The packed bed reactor has been assessed for CO\textsubscript{2} reduction over mixtures of commercial micron-sized Zn particles and ZnO particles [104]. The dilution of Zn with inert ZnO allowed for fast reaction rates and final Zn-to-ZnO conversions as high as 0.77 at relatively low temperatures ($T_i = 673$ K). Complete recovery of the ZnO particles after the reaction ended was possible. Comparison of the properties of the solar Zn oxidation system with the packed bed reactor characteristics listed in Table 3.1 reveals that the use of this reactor for the final process will face a number of constraints. Firstly, particle size analysis of samples collected from solar reactors presented in [28, 105] were fairly small with a volume based $d_{\text{mean}}$ between 0.0386 and 0.063 mm, far smaller than the particle sizes normally used in packed bed reactors (see Table 3.1). Operation with such small particles is typically avoided because of the associated high pressure drops and plugging issues. Additionally, the reaction is highly exothermic which in a reactor of poor heat transfer characteristics will result to large temperature gradients. Finally, continuous loading of Zn and unloading of ZnO particles will be necessary for particle recycling between the solar and non-solar step which is inherently inefficient in packed bed systems. Going to a moving bed reactor concept could deal with the latter but the problems of the high temperature gradients and high pressure drops would still persist.

The comparison presented in Table 3.1 points to the fluidized bed reactor as an attractive option to carry out H\textsubscript{2}O/CO\textsubscript{2} reduction by Zn particles. Firstly, it can operate in the particle size range expected for Zn particles produced in the solar reactor and can provide the efficient heat exchange needed for highly exothermic reactions to achieve adequate heat recovery and uniform temperature distributions throughout the bed. Additionally, fluidized bed reactors permit continuous operation which allows for efficient collection of ZnO particles after the reaction for transportation and treatment in the solar reactor. Disadvantages involve possible agglomeration, erosion of equipment, and low gas conversion
due to bubble formation and bypassing. The latter is an inherent problem of this reactor type and several techniques can be employed to circumvent it. These involve installation of multiple beds in series or addition of internal structures in the fluidized bed to break the bubbles and improve contacting [106]. A gas circulating system could also be envisioned that would allow for an increase in the gas conversion and thermal efficiency since less gas heating would be necessary. It should be noted that even though fluidization combines several advantages in theory it is often avoided in practice. The reason is the degree of complexity it involves which requires a lot of practical experience and know-how from the process designers in order to deal with the large uncertainty and avoid failures especially in scale-up [102]. Fluidization is sensitive to the particle morphology and properties and particularly to the particle diameter and density. For this reason the Geldart classification has been developed which correlates the particle morphology to the type of fluidization to be expected, ranging from very fine or cohesive powders which are hard to fluidize because of high interparticle forces (Group C) to large and/or dense particles which tend to give large, explosive bubbles, channeling or spouting behavior (Group D) [102]. Therefore, if the fluidized bed is chosen, care should be taken that the properties of the Zn/ZnO particles that are to be fed in the final reactor are well characterized by the time of the reactor design and that they remain more or less constant during reactor operation. In other words the design of the solar reactor will have to be finalized before the fluidized bed process can be designed in detail.

Another attractive option for the oxidation of Zn particles is the rotary cylinder reactor. Similarly to the fluidized bed, it can operate in a continuous mode and in the presence of fine particles. Additionally, it doesn’t face the issues of high pressure drops and particle agglomeration and allows for efficient gas-solid contacting that can result to high conversions. The main disadvantage of this reactor is its poor heat transfer characteristics which make heat exchange and recovery hard
and give rise to large temperature gradients. Therefore large heat exchanging surfaces are often necessary in such reactors.

3.1.2 Reactors for fluid-fluid reactions

The reaction oxidation of Zn in the gaseous or liquid form has also been investigated. Venstrom et al. [107] proposed a reactor concept similar to the aerosol flow reactor that operates above the Zn saturation point and considers the oxidation of \( \text{Zn}_\text{(g)} \) and its reaction on the reactor walls as the desired path rather than an unwanted side reaction. A thermodynamic analysis predicted that the high Zn-to-ZnO conversions achievable in this reactor counterbalance the energy penalty associated with the evaporation of Zn and can result to higher cycle efficiencies vis-à-vis a gas-solid reactor with low Zn-to-ZnO conversions. The main drawback of this reactor type is the lack of an efficient solution for the ZnO recovery from the reactor walls which will be necessary for practical application.

Laboratory studies have been performed with steam bubbling through molten zinc [108]. This concept was proposed for the oxidation of the product of the carbothermal reduction of ZnO which in contrast to the product of ZnO thermolysis can be readily collected in the liquid phase. This process didn’t exhibit kinetic advantages over the gas-solid processes as it was limited by the fast formation of a ZnO barrier which inhibited the contact of the reactive gas with the metal.

Overall, it has been shown that the oxidation of liquid and gaseous Zn is feasible. However, for these processes to counterbalance the investment of the latent heat required for the phase change and become attractive vis-à-vis the oxidation of solid Zn, they should first demonstrate potential of superior reaction kinetics combined with practical and economical process control.
3.2 Laboratory-scale experiments in a packed-bed reactor

3.2.1 Motivation

The comparison of key properties of common reactors for gas-solid reactions pointed to the rotary cylinder and the fluidized bed as the most promising candidates to carry out the H₂O/CO₂ reduction by Zn produced in a solar reactor. However, the final reactor design will require, especially in the case of the fluidized bed, a good characterization of the feed powder morphology which is not yet known since the solar reactor is still under development. Yet, initial lab-scale reactor experiments can be valuable for a first assessment of the reactive system and they do not necessarily need to be performed using the final contacting pattern [102]. For this intermediate step of the reactor development an easier to design, build and operate semi-batch type packed-bed reactor was used and the following points were evaluated:

a) Reaction rate and conversions of both gas and solid phase.

b) Development of temperature gradients in the reactor.

c) Sintering and agglomeration of particles.

d) Effect of different reactive atmospheres on reaction kinetics.

e) Effect of inert solids addition on reaction kinetics.

The information acquired from these small scale experiments are to be used for the development of the final reactor design.

3.2.2 Setup

A scheme of the experimental setup is shown in Figure 3.3.
Experimentation was performed with a 25 mm i.d. quartz tube vertically positioned in a tubular furnace (Carbolite, VST 17/250), containing a packed bed of mixtures of Zn and ZnO particles on top of a porous quartz disc. Two type-K thermocouples were placed at the inlet and outlet of the packed-bed. Mixtures of Zn (Sigma-Aldrich, 98+%, volume-based $d_{\text{mean}}= 6.7 \, \mu\text{m}$) and ZnO particles (Alfa Aesar, -325 Mesh, 99%, volume-based $d_{\text{mean}}= 5.45 \, \mu\text{m}$) were sieved to remove agglomerates. The inlet gas concentrations were varied in the range 0-75% H$_2$O-CO$_2$ and the total volumetric flow rates of reactants were set to 300 ml$_N$/min. Samples of 3000-9000 mg were used for the experiments which resulted in packed-bed heights of 0.45-1.65 cm that corresponded to average residence times of 0.139-0.54 s ($T= 678$ K). The ZnO mass fraction was varied between 33-67 wt% to to enhance kinetics [104] and increase the thermal inertia of the packed bed. A series of experiments was also conducted with particles (volume-based $d_{\text{mean}}= 43 \, \mu\text{m}$) obtained from the solar thermolysis of ZnO [28, 105] which contained 75 wt% ZnO as a result of both partial re-combination of Zn with O$_2$ during its production in the solar reactor and further
oxidation with atmospheric air afterwards. The sample size was ~6000 mg for all experiments with solar Zn-ZnO mixtures, which resulted in packed-bed heights of ~2.8 cm: more than double the height of a commercial mixture of the same weight, and corresponding to residence times of 3.8 s ($T = 678$ K). Due to lower critical fluidization velocity of this sample, the flow rate was reduced to 80 ml$_N$/min to prevent particle entrainment and fluidization. Figure 3.4 shows SEM pictures of the 50 wt% ZnO mixture prepared with commercial mixtures (Figure 3.4a) and of the 75 wt% ZnO mixture obtained by solar thermolysis of ZnO (Figure 3.4b). In the commercial sample, smooth solid Zn spheres are surrounded by the sub-micron ZnO particles. In the solar-made sample, sub-micron sized particles of Zn and ZnO create a porous foam structure with high surface area.

Figure 3.4. SEM picture of (a) 50 wt % ZnO mixture prepared with commercial particles, and (b) 75 wt % ZnO mixture obtained by solar thermolysis of ZnO.
The outlet gas composition was determined by mass spectroscopy (MS, Omnistar GSD301 O: sampling rate < 1 s⁻¹) and gas chromatography (GC, Varian CP-4900 Micro-GC two-channel system: sampling rate 0.5 min⁻¹) after condensing excess steam. Solid particle characterizations were performed after each experiment. Zn-to-ZnO conversions were determined by reacting ~500 mg of solid products in 1:1 solution of HCl acid and measuring the pressure change (Newport/Omega, PR33-C-1) due to H₂ production. Scanning electron microscopy (SmartSEM, Carl Zeiss Supra 55VP) was used to examine surface morphologies. Particle size distributions were analyzed by laser scattering (HORIBA LA-950 analyzer). BET surface areas were determined by N₂ absorption (Micrometrics TriStar 3000).

3.2.3 Results and discussion

A total of 33 experimental runs were performed for various sample sizes, Zn mass fractions, and reactive gas compositions with commercial and solar Zn-ZnO powder mixtures. Results from two representative runs with a 9000 mg sample of commercial 50 wt% ZnO and 6000 mg sample of solar 75 wt% ZnO are shown in Figure 3.5a and b, respectively. The reacting gas in both cases was 50% H₂O-CO₂. O₂ was purged from the system with an Ar flow and the packed-bed was heated to ~680 K. CO₂/H₂O mixtures were then introduced into the system after both the inlet (T\textsubscript{inlet}, dashed line) and outlet (T\textsubscript{outlet}, solid line) temperatures stabilized. High concentrations of syngas were immediately detected in the product gases as the gaseous reactants were converted to syngas. Nearly complete temporal conversions of H₂O and CO₂ to syngas were observed from 42 < t < 50 min and the competitive reaction between H₂O and CO₂ was not observed as reactions were limited by the gaseous reactants and not the available Zn (Figure 3.5a) for the larger part of the process. The rapid reaction resulted in heat released due to the exothermicity of the reaction, evidenced by a rapid
increase in $T_{\text{outlet}} = 900$ K. Small increases in $T_{\text{inlet}}$ were also observed as heat was conducted through the porous disc. Similar reaction mechanisms with solar powder (75 wt% ZnO) depicted in Figure 3.5b and commercial blends (50 wt% ZnO) were observed. However, a lower molar flow rate (80 mlN/min), implemented to prevent particle entrainment, resulted in lower syngas production rate and lower peak $T_{\text{outlet}}$. A H$_2$ peak was observed during the heat-up ($t \approx 20$ min) and can be attributed to reaction between Zn and absorbed moisture in the sample. The reaction nears completion after 10 min.
Figure 3.5. Inlet (dashed) and outlet (solid) temperatures and molar flow rates of CO (circles) and H₂ (squares) as functions of time for representative experimental runs with (a) a 9,000 mg sample of commercial blend containing 50 wt% ZnO exposed to 300 ml/min of 50% H₂O–CO₂, and (b) a 6,000 mg sample of solar powder containing 75 wt% ZnO exposed to 80 ml/min of 50% H₂O–CO₂. The markers represent the GC measurements and the lines the fit of the MS data.
**Zn Conversions**

The Zn conversion as a function of time was calculated by coupling high-temporal resolution MS measurements with accurate low-temporal resolution GC measurements for all experiments, except those with 75% H$_2$O where only GC measurements were used. The Zn conversions were determined as:

$$X_{Zn} = \frac{n_{ZnO}(t)}{n_{Zn,i}} = \frac{\sum\left(\hat{n}_{CO} + \hat{n}_{H_2}\right) \Delta t}{n_{Zn,i}}$$  \hspace{1cm} (3.1)

where $n_{Zn,i}$ and $n_{ZnO}$ denote the initial molar amount of Zn and the molar amount of ZnO produced, respectively. $\hat{n}_{CO}$ and $\hat{n}_{H_2}$ are the molar flow rates of CO and H$_2$, respectively, as determined from the MS and mass flow rate measurements, and $\Delta t$ is the time increment between measurements. The effects of wt% ZnO and sample size were also analyzed to maximize $X_{Zn}$. Temporal $X_{Zn}$ are shown in Figure 3.6 for 33-67 wt% ZnO and $m_{s,i} = 3000$ and 9000 mg. Slower initial conversion rates for $m_{s,i} = 9000$ mg versus $m_{s,i} = 3000$ mg (as seen with 50 wt% ZnO (dashed line)) correspond to slower reaction kinetics at the upper layers of the sample. These were initially exposed to lower concentrations of H$_2$O and CO$_2$ due high conversions of the reactive gases to CO and H$_2$ at the inlet of the packed-bed. On the other hand, low $X_{Zn}$ were observed with $m_{s,i} = 3000$ mg irrespective of ZnO wt%. This higher passivation of available surface area in the smaller samples in comparison to the larger samples can be attributed to the higher excess of reactive gas in the case of the former causing faster apparent reaction rates which in previous kinetic analyses have been linked to passivation of active surface area [44, 109]. Additionally, severe sintering was observed macroscopically at the inlet and outlet of the packed bed and where Zn-ZnO particles were in direct contact with the reactor, which could have contributed to the lower $X_{Zn}$ with $m_{s,i} = 3000$ mg where the ratio of external area to bulk volume of the particle bed is
higher and the impact of this sintering more significant. $X_{Zn} = 0.24$ at 33 wt% ZnO was significantly lower than $X_{Zn} = 0.77$ reported for reducing CO$_2$ [104], presumably due to higher reaction enthalpies and faster kinetics associated with steam [110]. Furthermore, both $X_{Zn}$ and conversion rates increase with wt% ZnO due to a decrease in the available Zn surface area resulting from an insufficient amount of ZnO. However, when considering the optimal wt% ZnO, larger amounts of ZnO inert support increase the pressure drop and the required sensible heat. For this reason, further investigations were pursued with 50 wt% ZnO.

Figure 3.6. Effect of ZnO on temporal Zn conversion for 50% H$_2$O-CO$_2$ and sample sizes of 9,000 and 3,000 mg.

The effect of H$_2$O concentration in the gaseous reactants was examined. Figure 3.7 shows $X_{Zn}$ as a function of time for 50 wt% ZnO with 25, 50, 75% H$_2$O-CO$_2$ and 100% CO$_2$. The markers represent the GC measurements which were used for the $X_{Zn}$ calculation of the run with 75% H$_2$O-CO$_2$. The results confirm previous observations that increased H$_2$O concentrations lead to higher reaction rates indicating
that the reaction is controlled by similar mechanisms [109]. However, no discernible trends are observed for overall $X_{Zn} (0.72-0.91)$.

![Figure 3.7. Temporal conversions of Zn for 50 wt% ZnO with 25, 50, 75% H$_2$O-CO$_2$ and 100% CO$_2$.](image)

Figure 3.7. Temporal conversions of Zn for 50 wt% ZnO with 25, 50, 75% H$_2$O-CO$_2$ and 100% CO$_2$.

Figure 3.8 shows the individual mean Zn conversion, $\bar{X}_{Zn}$, as a function of inlet gas concentrations for commercial 50 wt% ZnO with sample sizes of 9000 mg (circles) and 3000 mg (diamonds) and for solar 75 wt% ZnO (squares) with sample sizes of 6000 mg. The error bars were computed based on individual 95% confidence intervals, and the standard error for the means was 0.069, indicative of good reproducibility between experiments. Variances were due to heterogeneities in the raw Zn and ZnO, in the mixing of the particles, and in the packing of the bed. The individual overall $X_{Zn}$ for the solar samples are presented for two inlet gas concentrations for comparison. Confidence intervals were not added to the plots as experiments were performed only once due to a limited amount of solar Zn.
Figure 3.8. Individual mean Zn conversions as a function of the % H2O–CO2 for commercial 50 wt% ZnO, with sample sizes of 9,000 mg (circles) and 3,000 mg (diamonds), and for solar 75 wt% ZnO (squares) with sample sizes of 6,000 mg. Indicated are the error bars based on individual 95% confidence limits.

Decreasing the sample size resulted in a significant decrease in $\bar{X}_{\text{Zn}}$, well outside the 95% confidence limits of $m_{s,i} = 3000$ mg compared with $m_{s,i} = 9000$ mg, in agreement with Figure 3.6. For experiments with 100% CO2, $\bar{X}_{\text{Zn}}$ did not vary significantly with sample mass, consistent with previous observations for reducing CO2 to CO [104]. The introduction of steam in the system caused a decrease in $\bar{X}_{\text{Zn}}$, also observed in Figure 3.7, that was within the 95% confidence intervals for $m_{s,i} = 9000$ mg but not for $m_{s,i} = 3000$ mg. For both sample sizes, further increase of steam concentration caused a decrease in $\bar{X}_{\text{Zn}}$ with 50% H2O-CO2 and a subsequent increase with 75% H2O- CO2, especially pronounced for $m_{s,i} = 3000$ mg. This is thought to be due to the counteracting phenomena of higher reaction rates, causing more heat released, offset by the formation of more compact ZnO layers and
sintering [109]. For 25-50% H₂O-CO₂, the compact oxide layers passivate Zn particles, while at 75% H₂O-CO₂ the thermal stresses resulting from increased kinetics break the ZnO shell, forming cracks and holes and allowing the reaction to proceed. Increased $\bar{X}_{Zn}$ for the solar 75% ZnO is presumably due to the higher residence time, more available surface, more robust inert supports, and higher $w_{ZnO,i}$.

**Statistical Analysis**

Analysis of variance was used to compare the effects of Zn mass fraction and gas concentrations on $\bar{X}_{Zn}$. Because the interactions between Zn mass fraction and gas concentrations were significant ($p=0.0094$), individual $\bar{X}_{Zn}$ were compared using the Tukey multi-comparison procedure [111, 112]. Significant differences ($p \leq 0.0254$) between $\bar{X}_{Zn}$ were observed for $m_{s,i} = 3000$ mg with 100% CO₂ and 25-75% H₂O-CO₂. There was no significant evidence ($p \geq 0.5099$) to suggest $\bar{X}_{Zn}$ differences for $m_{s,i} = 3000$ mg with 100% CO₂ compared with $m_{s,i} = 9000$ mg with 0-75% H₂O-CO₂. $\bar{X}_{Zn}$ differences between $m_{s,i} = 9000$ mg with 0-75% H₂O-CO₂ concentrations were not significant except between 100% CO₂ and 50% H₂O-CO₂ ($p = 0.0398$). Significant $\bar{X}_{Zn}$ differences ($p \leq 0.0336$) were observed between $m_{s,i} = 3000$ mg and 9000 mg for 25-75% H₂O-CO₂. The $\bar{X}_{Zn}$ for $m_{s,i} = 3000$ mg and 50% H₂O-CO₂ was significantly different ($p \leq 0.0472$) from all other $\bar{X}_{Zn}$ indicative of a possible outlier.

**Solid Characterization**

Figure 3.9 shows the SEM pictures of samples collected from the middle of the packed-bed after reaction with 50% H₂O-CO₂ for commercial 50 wt% ZnO (Figure 3.9a) with $m_{s,i} = 9000$ mg, and for solar 75 wt% ZnO (Figure 3.9b). The smooth Zn spheres of Figure 3.4a
reacted to form hollow shells of Figure 3.9a that adhere to ZnO particles or, in the absence of a ZnO support, sinter together. The nanofilaments of Figure 3.4b reacted to form a similar porous structure of Figure 3.9b. The absence of significant sintering after the oxidation of the solar-made Zn corroborates the assumption of a robust support with ZnO.

Figure 3.9. SEM of products collected from the centre of the bed after reaction with 50% H₂O-CO₂ for (a) commercial 50 wt % ZnO, and (b) solar 75 wt % ZnO.

Figure 3.10 shows the SEM pictures of sample product for blends with 33 wt% ZnO (Figure 3.10a) and 67 wt% ZnO (Figure 3.10b) reacting with 50% H₂O-CO₂. The inadequacy of the support led to the passivation of the Zn spheres, whereas increasing the ZnO support
resulted to more frequent cracking of the ZnO shell surrounding the particles which can explain the higher conversions obtained with these samples seen in Figure 3.6.

The BET specific surface areas of the initial Zn and ZnO particles were 5.94 and 2.10 m²/g, respectively, which decreased to 1.82 m²/g after the reaction of 75 wt% ZnO with 50% H₂O-CO₂. The solar Zn had a much higher initial surface area of 21.98 m²/g, consistent with the highly porous “sponge-like” structures observed in the SEM analysis (Figure 3.4b). After reaction with 50% H₂O-CO₂, the specific surface area decreased to 13.27 m²/g, indicative of sintering.
3.3 Summary and conclusions

The second, non-solar step of the Zn/ZnO solar thermochemical cycle to produce syngas from CO$_2$ and H$_2$O reduction has been investigated in laboratory-scale experiments to provide a basic evaluation of the reactive system and gather information which are to be used in the development of the final reactor design. The experiments were performed in an easy to design, build and operate packed bed reactor using Zn-ZnO mixtures containing 33-67 wt% ZnO reacting with gas flows containing 0-75% H$_2$O in CO$_2$. The reaction rate and final reaction extent increased with wt% ZnO, and high overall Zn conversions of 0.72-0.91 were observed over a range of H$_2$O/CO$_2$ concentrations. Competitive reactions between the H$_2$O and CO$_2$ were not observed as the gaseous flow rate, not solid reactants, limited the reactions for a great part of the process resulting to H$_2$/CO ratios in the syngas which corresponded to H$_2$O/CO$_2$ ratios in the inlet flows. Higher reaction rates were observed with H$_2$O% in the gaseous mixtures, which combined with the reaction exothermicity, resulted in higher maximum bed temperatures which could enhance both local sintering and cracking of the ZnO shell surrounding the Zn particles. Zn-ZnO mixtures produced from solar thermolysis of ZnO were also tested under similar conditions and proved to be highly reactive yielding overall Zn-to-ZnO conversions of ~0.96 without any additional ZnO dilution. The partial re-oxidation of Zn-to-ZnO during the solar Zn production step could therefore readily provide the inert support needed for efficient H$_2$O/CO$_2$ splitting to be achieved in the second step of the cycle.

The reactor used was adequate for a first assessment of the reactive system in laboratory scale experiments but would be unsuitable for industrial application due to excessive pressure drops caused by the small particle size, large temperature gradients resulting from the high exothermicity of the reactive system combined with low heat exchange properties and inefficient particle feeding. The rotary type reactor and the fluidized bed reactor have been recognized as the most promising
reactor types. Both of them can operate in the particle size range expected for Zn particles produced in the solar reactor and allow for continuous feeding of the solid reactant for transportation and treatment in the solar reactor. The fluidized bed offers additionally good heat exchange and almost isothermal operation conditions but suffers from high agglomeration, erosion of equipment, high complexity in the process design and control and low gas conversion due to bubble formation and bypassing. The latter can be dealt with by installing multiple beds in series, internal bubble-breaking structures or recycling the gas to achieve high conversions. On the other hand the rotary cylinder reactor doesn’t face the issues of high pressure drops and particle agglomeration and allows for efficient gas-solid contacting that can result to high conversions but suffers from poor heat transfer characteristics which make heat exchange and recovery hard and give rise to large temperature gradients.

Before the reactor design is finalized, the morphology and reactive behavior of the feeding particles have to be better understood and characterized. However, the solar reactor that will produce the particles is still under development and their final characteristics are therefore unknown. In the meantime, surrogate materials could be used to understand the effect of particle morphology and experimental conditions on Zn oxidation. More work should be dedicated in understanding the influence of the presence of inert ZnO in the solid reactant which in this chapter was shown to have a dramatic effect on the reaction rate and final conversion of Zn and can significantly affect the overall efficiency of the process.
4 Effect of the presence of inert diluents on Zn oxidation

The fraction of ZnO in the solid product leaving the solar reactor after the thermolysis step generally varies with a solar reactor/quencher design and experimental conditions. In Chapter 3 the importance of the presence of inert ZnO in a starting Zn-ZnO blend was demonstrated as a factor that can dramatically increase the reaction rate and final conversion of Zn. Due to the high energy consumption associated with the production of solar Zn, the final Zn conversion and thereby the amount of Zn returned back to the solar reactor without being oxidized to fuel has adverse impact on both chemical and heat utilization efficiencies. Therefore, dilution of Zn with ZnO can be used as an optimization tool for the cycle efficiency either by controlling the extent of re-oxidation allowed in the production process of solar Zn and/or by applying additional mixing with inert diluent prior to the fuel production step. However, no kinetic study to this day has systematically examined the effect of the composition of the starting solid mixture on the intrinsic kinetics of Zn oxidation. In this chapter, the effect of solid inert dilution on CO₂ splitting is experimentally investigated as a first step towards the development of a reliable kinetic model that is to be used for scale-up of the thermochemical cycle and optimization of its overall efficiency.

4.1 Theoretical background

In order to explain the effect of inert diluents on Zn oxidation it is necessary to understand the mechanisms that govern the oxidation of undiluted Zn. Therefore, a literature review on Zn oxidation was conducted and the main proposed reaction mechanisms were acknowledged. Additionally, the complex and sensitive dependence of Zn asymptotic conversion on several experimental factors is summarized, as reported in previous works, and the positive effect of ZnO dilution on Zn conversion is recognized. Finally, previous attempts in literature to explain the positive effect of the presence of inert solids on other gas-solid reactions are presented and their correlation to Zn oxidation is discussed.

4.1.1 Kinetics of Zn oxidation

Proposed mechanisms in the absence of solid diluents

Zn oxidation is a complicated and still poorly understood process. Several studies have been performed on the reaction of Zn of various morphological characteristics with different gaseous oxidants under a vast range of experimental conditions resulting to the development of various often contradicting oxidation theories. Here, a selection of works is presented with the purpose of summarizing the main governing mechanisms of Zn oxidation proposed.

Vernon et al. [113] studied the oxidation of Zn in air at temperatures ranging from 298 K to 673 K. Four types of samples were prepared using a 700 μm thick Zn sheet which was cut and subjected to different kinds of pre-treatment involving abrasion or etching with or without annealing. Even though all experiments were conducted below the Zn melting point (692 K), Zn volatilization was observed under vacuum or inert atmospheres in temperatures as low as 548 K in samples where no protective oxide layer was present as a result abrasion or pretreatment in air. The weight change held a logarithmic relationship
with time with very good agreement above and only approximate agreement below 498 K. It was suggested that the reaction is controlled predominantly by diffusion of oxygen atoms inwards which is promoted by the existence of interstitial Zn ions in the ZnO lattice. The oxidation rate of the etched samples exhibited a decrease with increasing temperature in the range of 423 to 498 K and the reverse effect below and above this range. The authors attributed this phenomenon to the already formed amorphous ZnO layer surrounding the particle becoming more compact with temperature between 423- 498 K and thereby introducing an indirect restraining effect on the oxidation rate which cancels out the normal promoting effect of temperature. Above a certain temperature the film crystallization becomes very fast resulting to an entirely crystalline film above 498 K at which point the restraining effect disappears and the promoting effect of temperature on the reaction rate is expressed.

Moore et al. [114] studied the oxidation of 127 μm thick Zn foil in oxygen at temperatures between 573-673 K reporting formation of oxide layers as thick as 120 nm at the highest temperature. They observed that the rate of the ZnO layer growth follows a logarithmic equation below 643 K and a parabolic rate law above this temperature. In the latter case the rate constant was significantly dependent on the O2 concentration which led to the suggestion of adsorption of oxygen at the ZnO surface as the controlling mechanism. The probable steps of the oxide film growth include (i) the activated adsorption of O2 as O atoms on the ZnO surface, (ii) conversion of adsorbed O atoms to O- ions and Zn2+ diffusion next to the O- with a concurrent formation of a vacant Zn2+ structure site, (iii) Zn2+ migration from the metal to the vacancy resulting to a formation of a new layer of ZnO. It is additionally mentioned that the diffusion of oxygen to the underlying metal along grain boundaries in the ZnO film is another mechanism that may have to be considered.
Clarke et al. [115] investigated the oxidation of Zn with mixtures of CO₂/CO/Ar in a silica tube consisting of various temperature regions ranging from 1173 K to 973 K. For temperatures below 1073 K the reaction rate exhibited a linear dependence on the excess Zn partial pressure which could be explained by two rate controlling processes: (i) adsorption of Zn from the unsaturated vapor phase in the ZnO surface or (ii) adsorption of Zn into the ZnO lattice in the form of interstitial Zn ions which during the ionization process produce an equal amount of surface sites where CO₂ can be adsorbed.

Nakamura et al. [116] studied the oxidation of Zn nanoparticles with 10 nm < d < 50 nm by transmission electron microscopy in air atmosphere and a temperature range of 383 - 423 K. They observed an initial rapid reaction which was accompanied by the formation of voids at the Zn/ZnO interface and leveled off after the oxidation layer reached a certain thickness. The critical thickness was identified at 7 nm for 383 K and 10 nm for 423 K. The mechanism proposed is outward Zn ion migration from the metallic core, through the oxide layer, to the outer part of the ZnO film where the reaction and formation of a new ZnO layer takes place. This leads to vacancy formation in the particle core which in the case of fully reacted small particles (d < 20 nm) results to the formation of hollow ZnO particles. No hollow particle formation was observed for the oxidation of larger Zn particles due to the creation of a thick oxide layer resulting to incomplete conversions.

Enrst et al. [36] studied the hydrolysis of Zn nanoparticles with d_{BET} = 164 nm in a thermogravimetric balance at temperatures between 603 and 633 K and reactive atmospheres containing 10-50% H₂O in Ar. They reported an initial reaction regime, which corresponded to ~10% of the overall reaction extent and exhibited fast reaction rates with a half-order dependence on the water vapor mole fraction. The following second step exhibited a much slower reaction rate, which followed a parabolic rate law and was virtually independent of the water vapor mole fraction. In their proposed mechanism, the initial step is a result of
the presence of a number of interstitial Zn$^{2+}$ in the outermost layer of the particle which reacts rapidly with H$_2$O. The half-order dependence on H$_2$O vapor is assigned to the reaction rate being controlled by the dissociation of the water molecules on the Zn/ZnO surface. Once the outer Zn$^{2+}$ ions are consumed the reaction becomes limited by the diffusion of Zn ions outwards through the formed ZnO film. This is justified by the low observed dependence of the reaction rate on the H$_2$O vapor mole fraction and the parabolic temporal behavior of the sample’s weight gain combined with previous reports that the diffusion coefficient of Zn$^{2+}$ in ZnO is much higher than that of O$^-$ at this temperature range.

Loutzenhiser et al. [44] investigated CO$_2$ splitting in a thermogravimetric balance using Zn particles with d$_{\text{mean}}$ = 11.4μm which were reacted with 0.5-75 %CO$_2$ in Ar in a temperature range of 654-754 K for isothermal experiments. A fast initial reaction regime was observed which was followed by a slower step and finally to impediment of the reaction before complete conversion of Zn-to-ZnO. The reaction steps assumed were mostly consistent with the metal oxidation theory[117]. The fast step comprised (i) CO$_2$ adsorption on the surface, oxide nuclei formation, and desorption of CO, (ii) nuclei growth and (iii) formation of a uniform oxide layer. Once the oxide layer is formed, the reaction continues by migration of Zn cations outwards and/or oxygen anions inwards through the oxide lattice while electrons move independently from the interface to the particle surface. The novelty of this work is introduced with the observation that during dynamic runs with rates of 20K/min, passivated, partially-reacted Zn samples would get reactivated after 860 K and reach almost full conversion at 1173 K. This lead to the formation of the mechanism described in Figure 4.1 which includes

f) fresh Zn particle exposed to CO$_2$

 g) interface controlled regime where the lateral nuclei growth apart from Zn solid state diffusion is enhanced by sublimation of Zn and deposition/adsorption on the nuclei
h) ionic diffusion controlled reaction
i) development of cracks on the ZnO layer caused by high Zn$_{(g)}$ partial pressure followed by interface-controlled reaction of Zn$_{(g)}$ and CO$_2$.

Figure 4.1. Schematic depicting the stages of Zn oxidation with CO$_2$ comprising (a) initial Zn particle exposed to CO$_2$, (b) interface-controlled reaction, (c) diffusion-controlled reaction and (d) development of cracks followed by interface-controlled reaction of Zn$_{(g)}$ and CO$_2$ [44].
This study adds two new elements to the existing proposed mechanisms: (i) the growth of ZnO nuclei during the fast part of the reaction can be enhanced by Zn sublimation from the bulk and condensation/adsorption on the nuclei surface even below the Zn melting point (Figure 4.1(b)) (ii) stressed induced cracking of the ZnO layer can occur under certain conditions and can provide an alternative path to ionic diffusion for the continuation of the reaction after the uniform compact layer has been formed even in cases where the sample has already been passivated.

The numerous and often contradicting proposed reaction steps encountered in the undiluted Zn oxidation studies elucidate the complexity of the reaction. An effort to summarize the possible steps governing the reaction is presented, divided in three main categories:

a) Reaction before formation of continuous ZnO film: The reaction steps include adsorption of gaseous reactant and diffusion on the Zn surface, reaction with solid Zn resulting to oxide nuclei formation and lateral growth, and finally desorption of the gaseous product in the cases where CO₂ or H₂O is used as the oxidant. At temperatures in the vicinity of the Zn melting point the reaction can also proceed through Zn present on the nuclei surface as a result of Zn condensation/adsorption after evaporation from the bulk. This can result to both lateral and vertical growth of ZnO nuclei. The latter doesn’t contribute to the formation of a continuous ZnO layer.

b) Reaction after formation of continuous ZnO film: Once a continuous, compact ZnO layer is formed the reaction proceeds through diffusion of Zn ions outwards, and/or oxygen ions inwards. The diffusion rate will strongly depend on the morphology (crystallinity, compactness e.t.c.) of the ZnO film which is a factor of oxidation temperature, oxidant type and concentration and initial Zn morphology. The reported rate controlling steps include the oxidant adsorption
on the oxide surface, oxidant dissociation, rate of ionic diffusion, desorption of gaseous product. Once a critical oxide layer thickness is reached the reaction stops. The critical thickness depends on the temperature and the ZnO film morphology. If grain boundaries are present on the ZnO layer the reaction can also proceed through O\textsubscript{2} diffusion along the boundaries to the underlying metal.

c) **Reaction after cracking of impervious ZnO film**: The build-up of stresses can cause cracking of the ZnO layer. In these cases the reaction proceeds similarly to the reaction before formation of the impervious ZnO film until a new continuous film is formed.

The above summary provides a basis of possible mechanisms that have to be considered when investigating Zn oxidation in the presence of inert diluents.

**Asymptotic conversion in Zn oxidation**

It has been observed that Zn oxidation commonly exhibits asymptotic conversion that generally varies with experimental conditions such as temperature [44, 109, 118], oxidant concentration [44, 104, 109], and starting Zn particle size[119]. While decreasing particle size of Zn resulted in expected increase in the asymptotic conversion [119], some of the reported findings summarized in Table 4.1 appear to be conflicting which introduces additional difficulty in interpreting phenomena governing this complex gas-solid reaction.

Reasons leading to discrepancy in the observed effects of experimental conditions on the asymptotic conversion could be classified into two broad categories:

1. **Experimental artifacts**. Studies were generally performed in:
a. TGA setups that have not been validated for the absence of heat and mass transfer intrusion on the intrinsic kinetics [44, 109, 118, 120].

b. Non-isothermal packed beds, where the effects of uncertain flow pattern together with temperature and concentration gradients could have confounded intrinsic effects [104, 110].

2. Nature of the reacting material: The source of solid Zn ranged from commercially available pure powders to Zn-ZnO blends produced in solar reactors [54, 118] or their surrogates [31]. These starting materials differed not only in particle size distributions but very likely in morphology and composition also, thereby expanding the list of factors that could have contributed to differences in the observed reactivity.

The studies discussed so far have not considered the nature of the starting mixture as a specific parameter. However, a few, including the study presented in Chapter 3, have pointed out to the presence of inert ZnO in a starting Zn-ZnO blend as to yet another factor that can dramatically affect the final conversion of Zn. The samples of Zn intentionally diluted with ZnO [104, 110] as well as in situ generated Zn-ZnO mixtures produced in a solar reactor [118] have exhibited higher asymptotic conversions compared to pure Zn that generally increased with an increase in the initial ZnO content.
Table 4.1. Summary of observed effect of $T$, %$CO_2$ and %$H_2O$ on final conversion as reported in various Zn-oxidation studies.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Setup/ mode</th>
<th>Zn source</th>
<th>Ranges</th>
<th>Effect on $X_{Zn}$ with increasing:</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>$T$, K</td>
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<td>Increases</td>
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<td>683-803</td>
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<tr>
<td>[118]</td>
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<td>50</td>
<td>No effect</td>
</tr>
<tr>
<td></td>
<td>TGA/ dynamic</td>
<td>Solar$^b$</td>
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</tr>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>TGA/ constant SP</td>
<td>Solar$^c$</td>
<td>603-773</td>
<td>Increases</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TGA/ dynamic</td>
<td>Solar$^c$</td>
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<td>50, 100</td>
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<td>[109]</td>
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<td>673-748</td>
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<td>Effect on $X_{\text{Zn}}$ with increasing:</td>
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<tr>
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<td>Commercial$^e$</td>
<td>680</td>
<td>25-100</td>
</tr>
</tbody>
</table>

$^a$ Produced with solar ZnO reduction; estimated 10-35 wt% ZnO  
$^b$ Produced with solar ZnO reduction; estimated 52 wt% ZnO  
$^c$ Produced with solar vapo-condensation of commercial Zn; estimated 13 wt% ZnO  
$^d$ Sample containing 33 wt% ZnO  
$^e$ Sample containing 50 wt% ZnO
4.1.2 Presence of inert solids in gas-solid reactions

There have been only a few works in literature explicitly dedicated on the effect of solid diluent addition on the reaction rate and asymptotic conversions of gas-solid reactions which are subjected to structural changes during the reaction [121-124].

The first paper published on this topic [121] examined the case where the solid product has a higher molar volume than the molar reactant causing the particles to swell as the reaction progresses.

The analysis is based on the particle-pellet model which is depicted on the left column of Figure 4.2 for the absence of inert solids and on the right column for the presence of inert solids. Both reactive and inert particles contained in the pellet are assumed to be spherical and non-porous while a porous solid product grows around the reactive particles as the reaction progresses. The swelling of the particles causes a decrease in the porosity, thereby causing the effective diffusivity of the gases to decrease. In cases of high molar volume ratio, eventually pore closure takes place and the reaction stops resulting in asymptotic conversion. No sintering is assumed to take place during the reaction.

In the same paper a mathematical model is presented to describe the effect of inert diluents on the kinetics of non-catalytic gas solid reactions in terms of temporal solid conversion and gas uptake which can be applied to reactions which level off before completion due to pore plugging. The results show that pore plugging can be prevented by the addition of inert solids and better utilization of the solid can be achieved. This is of particular importance in cases of expensive solid reactants. The model was qualitatively evaluated using data from the \( \text{SO}_2 \)-dolomite reaction. These results confirm the model predictions that final reaction extents time for pore closure are increased by the presence of inert diluents in this type of reactions.
Since ZnO has a higher molar volume than Zn the mechanism proposed in these studies provides a plausible explanation for the extreme positive effect of inert dilution on Zn oxidation. However, as seen in Chapter 3, the Zn asymptotic conversion depends not only on the diluent mass fraction but also on the initial mass of the sample and the type of gaseous oxidant both of which can’t be explained by the proposed model. Therefore, it is possible that avoidance of pore plugging contributes to the positive effect of Zn dilution but an extension of the mechanism will be needed to describe the whole range

Figure 4.2. Particle-pellet model in case of no added inert particles (left) and in case with added inert particles (right) [121].
of phenomena observed during the Zn oxidation under the presence of inert solids.

### 4.2 Motivation

Due to the thermodynamic constraints, direct ZnO thermolysis (Eq. (2.1)) requires temperatures as high as 2235 K that are well above the normal boiling point of Zn (1180 K) [125, 126]. Since the product Zn vapor readily recombines with O₂ within a wide temperature range, high Zn yield necessitates both fast quenching and dilution of the product mixture with a substantial amount of inert gas [127]. This imposes a major technical challenge. As a result, the product leaving the solar thermolysis reactor/quencher, i.e., the feed for the oxidation step, generally contains a substantial amount of ZnO. The molar fraction of ZnO in the final product has been observed to be as low as 6 mol % [127] and as high as 85 mol % [28], depending on reaction conditions and inert gas/Zn(g) dilution ratio. On the other hand, as seen in section 4.1.1, it has been observed that Zn oxidation to ZnO (Eq. (2.3)) commonly exhibits an asymptotic conversion that generally varies with experimental conditions and can be dramatically affected by the presence of inert ZnO in a starting Zn/ZnO. The samples of Zn intentionally diluted with ZnO [104, 110] as well as in situ generated Zn/ZnO mixtures produced in a solar reactor [118] have exhibited higher asymptotic conversions compared to those of pure Zn. Considering that the efficiency of the overall splitting cycle depends on the conversions achieved in both reaction steps [107], evaluating the ZnO diluent effect is a crucial step towards a reliable kinetic model that is to be used for scale-up and optimization of the cycle efficiency. Specifically, it is necessary to understand to which extent it may be beneficial to not fully reduce ZnO in the solar reactor and/or allow recombination of Zn and O₂ in the quencher by reducing the amount of inert quench gas. As a result, the energy input into the process could be
optimized to yield not the maximum amount of Zn possible but the amount that could be fully exploited for fuel production.

4.3 Experimental part

4.3.1 Setup

Materials
In order to ensure abundant quantity, well-characterized properties, and flexible ZnO content in starting reacting material, blends of commercial Zn (Sigma-Aldrich>98%) and inert powders were used in contrast to solar Zn-ZnO product having a preset composition. Three types of ZnO and one type of Al₂O₃ were used as diluents to investigate the effect of different particle morphology and physico-chemical properties on the Zn conversion. For comparison reasons, a few experiments were performed using a Zn-ZnO powder produced in a solar reactor [28] which contained 61 wt% ZnO as measured at the production date but had further oxidized to 81.9 wt% ZnO when it was used for this study. The Zn content in this sample was determined by saturating a given amount of sample with 1:1 aqueous solution of HCl and measuring the amount of evolved H₂ via the corresponding pressure change (Newport/Omega, PR33-C-1). Raw materials were analyzed for particle size distribution (HORIBA LA-950 laser scattering analyzer with water as dispersion medium), BET area (Micrometrics TriStar 3000 N₂ absorption analyzer), and apparent native morphology (SEM, Hitachi TM-1000). The pertinent properties are summarized in Table 4.2.
Table 4.2. Key characteristics of used solid materials.

<table>
<thead>
<tr>
<th>Name</th>
<th>$d_{\text{mean,vol}}$, $\mu$m</th>
<th>BET $m^2/g$</th>
<th>Macroscopic and SEM observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn dust</td>
<td>6.7</td>
<td>1.5</td>
<td>Round, smooth particles, agglomerated</td>
</tr>
<tr>
<td>ZnO Alfa</td>
<td>5.45</td>
<td>2.71</td>
<td>Sponge-like structure, highly agglomerated, compressible</td>
</tr>
<tr>
<td>ZnO Grillo</td>
<td>6.53</td>
<td>2.92</td>
<td>Very fine needles, highly agglomerated, compressible</td>
</tr>
<tr>
<td>ZnO Fluka</td>
<td>15.63</td>
<td>5.15</td>
<td>Sponge-like structure, highly agglomerated, compressible</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>80.84</td>
<td>70.64</td>
<td>Large particles with cracks, high flowability over quartz, not agglomerated, not compressible</td>
</tr>
<tr>
<td>Solar Zn</td>
<td>40</td>
<td>21.98</td>
<td>Porous agglomerates of fine individual grains</td>
</tr>
</tbody>
</table>

As shown in Figure 4.3, the volume based size distributions and mean particle sizes ($d_{\text{mean}}$) of ZnO particles acquired from Alfa and Grillo matched closely the distribution of the Sigma-Aldrich Zn particles. The ZnO particles acquired from Fluka had the mean size of the same order of magnitude as the Sigma-Aldrich Zn but somewhat wider size distribution. The Al$_2$O$_3$ particles were considerably larger compared to the rest.
Figure 4.3. Volume-based particle size distributions of raw Sigma Aldrich Zn, Solar Zn, and four inert diluents used in this study: three ZnO materials and one Al\(_2\)O\(_3\).

The SEM pictures of the Zn sources and inert diluents are shown in Figure 4.4 and Figure 4.5, respectively. Figure 4.4 indicates the solar Zn comprised porous agglomerates of finer individual grains, thereby explaining its larger mean particle size despite its considerably higher BET area compared to the Sigma-Aldrich Zn (Table 4.2). As shown by Figure 4.5 a, the high BET area of even coarser Al\(_2\)O\(_3\) particles originated from the macro- and meso-porosity due to cracks traversing partially exfoliated layered structure.
Figure 4.4. SEM pictures of (a), (b) Sigma-Aldrich Zn particles and (c), (d) solar Zn particles produced in the solar reactor as described in [28].
Figure 4.5. SEM pictures of (a) Al$_2$O$_3$ particles and ZnO particles purchased from (b) Alfa, (c) Grillo and (d) Fluka.

**TG Analysis**

Oxidation kinetics of Zn blended with the inerts was investigated under isothermal conditions in a thermogravimetric system (TG, Netzsch 409 CD/STA). Prior to experimentation the setup was evaluated using mass and flow independence studies, explained in detail in Appendix A, and was proven to be free of heat and mass transfer intrusion in the range of experimental conditions used in the present campaign. Most of the blends were prepared by shaking and stirring constituents in a quartz vial for ~3min with three intermittent breaks made to crash agglomerates using a spatula. A limited number of blends were prepared by making a slurry of constituents in ethanol which was then homogenized by a mortar in a pestle into a homogeneous paste and
left to dry out prior to its use in the TG. The blends were placed on Al₂O₃ crucibles supported by an alumina rod that incorporated an S-type thermocouple. The reaction chamber was initially flashed with Ar (PanGas, purity 99.999%) to ensure O₂ levels below 300 ppm, and then heated to a prescribed setpoint temperature in Ar at the rate of 10 K/min. Once the temperature reached steady-state, a mixture of CO₂ (Pangas 4.5, g 99.995%) and Ar commenced into the TG. The total flow rate of CO₂ and Ar was set to 152 ml/min. All experiments were performed at ambient pressure (~1bar). The product gases were analyzed by gas chromatography (2-channel Varian Micro GC, equipped with a Molsieve-5A and a Poraplot-U columns). The majority experiments were reacted with 15% CO₂ in the temperature range of 623-673 K (below melting point of Zn).

**Zn Conversion**

The conversion, $X_{Zn}$, represents the fraction of Zn reacted to ZnO. It is calculated, similarly to equation (2.10) using the mass gain, $\Delta m$, recorded from the TG, the initial sample mass, $m_{s,i}$ and the initial mass fraction of ZnO, $w_{ZnO,i}$ according to equation:

$$
X_{Zn} = \frac{n_{Zn,i} - n_{Zn}}{n_{Zn,i}} = \frac{\Delta m/(M_{ZnO} - M_{Zn})}{m_{s,i} \left(1 - w_{ZnO,i}\right)/M_{Zn}}
$$

(4.1)

where $n_{Zn}$ and $n_{Zn,i}$ represent the temporal and initial number of moles of Zn, respectively, while $M_{Zn}$ and $M_{ZnO}$ the molar mass of Zn and ZnO, respectively.

4.3.2 Results

**Effect of ZnO dilution**

Effect of ZnO dilution on the CO₂ reaction with the Sigma-Aldrich Zn was investigated using the ZnO material acquired from Grillo. 8mg
aliquots of the Zn were dry mixed in various ratios with the ZnO and then contacted with 15% CO₂-Ar at 623 K. The results are shown in Figure 4.6, indicating that the fraction of the Grillo ZnO in the starting blend has a profound effect on both oxidation rate and the final conversion of the Sigma-Aldrich Zn. Remarkably, while the non-diluted Zn was essentially passive for the reaction, the Zn diluted by 85 wt% ZnO reacted almost completely. In addition, poor run-to-run repeatability during the second stage of the reaction with 50 wt% ZnO blends was not observed with 85 wt% ZnO blends. These results are consistent with previous observations of CO₂ [104] and H₂O/CO₂ reactions with Zn-ZnO mixtures in a packed bed [110].

![Figure 4.6](image)

Figure 4.6. Effect of the ZnO (Grillo) dilution on the Zn (Sigma-Aldrich) conversion: samples prepared by dry mixing and reacted with 15% CO₂ – Ar at 623 K. The dashed lines designate repeated experiments.

The SEM pictures of the material remaining in crucible after the experiment with the non-diluted Zn that showed no reaction were compared with those of the starting Zn Sigma-Aldrich in Figure 4.7.
Although it seems that the grain size somewhat increased during the experiment due to sintering, no substantial morphological difference between the starting and the product materials could be observed. The product material was then dry mixed with the ZnO to 50 wt% dilution and the resulting blend was subjected to the same experimental procedure and conditions as the 50% ZnO blends represented in Figure 4.6 were. The conversion, however, was negligible which implied that (a) the presence of ZnO in the experiments shown by Figure 4.6 prevented passivation of the Zn and (b) once passive for the reaction, the Zn could not be reactivated by the presence of ZnO alone at 623K. It has been reported elsewhere, however, that the activity can be recovered by increasing reaction temperature and that at 673 K the Sigma-Aldrich Zn does react in the absence of any ZnO diluent reaching the asymptotic conversion of ~0.2 [44].
Figure 4.7. SEM pictures of Zn (Sigma-Aldrich) before and after the experiment with 15% CO$_2$-Ar at 623 K and no ZnO added.
**Effect of temperature**

Figure 4.8 illustrates the effect of temperature on the reaction kinetics investigated with 50 wt% Zn (Sigma-Aldrich)-ZnO (Grillo) blends and 15% CO$_2$-Ar gas mixtures. Both reaction rate and the final conversion increase with temperature. Markedly, ~95% of Zn was converted to the product at 673 K, implying that reacting Zn above its boiling point [107, 128] is not the only path towards improved utilization of Zn for fuel production. The increase in asymptotic conversion with temperature is consistent with the results obtained using non-diluted Zn and it has been attributed to the rupture of the passivating ZnO layer at higher temperatures which facilitates the exposure of Zn to the oxidants [44].

![Figure 4.8](image.png)

**Figure 4.8.** Effect of temperature on conversion of the Zn (Sigma-Aldrich) diluted with 50 wt% ZnO (Grillo) by dry mixing and reacted with 15% CO$_2$ – Ar. The dashed lines designate repeated experiments.

The SEM pictures shown in Figure 4.9 support this explanation by indicating the presence of hollow particles in the product obtained at
673 K but not in the one obtained at 623 K. Finally, Figure 4.8 indicates remarkable run-to-run repeatability at 648 K as compared to the significant discrepancy observed between the final stages of two runs performed at 623 K.

Figure 4.9. SEM pictures of products obtained after experiments at 623 K (a) and 673 K (b) described in Figure 4.8.

Effect of CO₂ concentration

The effect of CO₂ concentration has been reported for non-diluted Sigma-Aldrich Zn at temperatures of 673 K and higher [44]. Those results have shown that the reaction rates increased with an increase in CO₂ concentration but that the asymptotic conversion decreased. In
contrast, solar-generated Zn-ZnO mixtures have shown no effect on the asymptotic conversion[118]. The latter is in agreement with the results obtained at 648 K with dry mixed 50 wt% Zn (Sigma-Aldrich)-ZnO (Grillo) blends that are shown in Figure 4.10.

![Figure 4.10](image_url)

Figure 4.10. Effect of CO₂ concentration on conversion of the Zn (Sigma-Aldrich) diluted with 50 wt% ZnO (Grillo) by dry mixing and reacted at 648 K. The dashed lines designate repeated experiments.

**Effect of inert diluent source and type**

Albeit only for a specific type of ZnO particles, the effect of ZnO dilution on the kinetics of Zn oxidation has been reported in the past [104, 110, 118]. However, possible effects of morphology and physico-chemical properties of various diluents have not been reported. For this reason, the effect of four different diluents described in Table 4.2 and Figure 4.5 was explored by testing their 50 wt% blends with Zn (Sigma-Aldrich). These blends were all prepared by dry mixing and then exposed to 15% CO₂ at 648 K. The results are shown in Figure 4.11 where the symbols specify inert source and dashed lines designate
experiments that were repeated. As shown by this figure, all but one ZnO blend (Alfa) exhibited asymptotic conversions of ~0.8 while Zn blended with Al₂O₃ barely reacted at all. It should be noted that the Al₂O₃ material exhibited free-flowing and had a tendency to segregate from Zn particles during blending. It appears that the performance difference between Grillo and Alfa ZnO diluents should be attributed to poor repeatability of the results obtained with Alfa ZnO blends rather than to the inherent difference in the ZnO source. In addition, this figure demonstrates that all the ZnO sources tested could provide similar asymptotic conversions although the ZnO Fluka blend exhibited markedly faster kinetics.

Figure 4.11. Effect of inert diluent source on the conversion of Zn (Sigma-Aldrich) diluted to 50 wt% by dry mixing and reacted with 15% CO₂ – Ar at 648 K. The dashed lines designate repeated experiments.

**Effect of blend preparation method**

Blending solids into a homogeneous mixture is a challenging task which is governed by the bulk flow (free-flowing vs. cohesive) and
physico-chemical surface properties of the ingredients as well as by their shape and size distribution [129]. Empirical observations have suggested that solids similar in size, shape, and density are more likely to form uniform mixtures while free-flowing powders generally tend to segregate[129]. Therefore, it was reasonable to consider variable homogeneity of the blends achieved with different diluents as culprit for the performance discrepancy observed in Figure 4.11.

In order to explore whether an alternative powder mixing method would affect the run-to-run repeatability and reaction kinetics, a 50 wt% Zn (Sigma-Aldrich) – ZnO (Alfa) mixture was prepared by dispersing the ingredients in ethanol and then homogenizing the resulting slurry with a mortar and pestle into a paste. The Alfa ZnO was chosen as diluent because it demonstrated poorer run-to-run repeatability than the ZnO material acquired from Grillo (Figure 4.11). The paste was left to dry and then reacted at 648 K with 15% CO₂-Ar to be compared in Figure 4.12 with the performance of the same composition blend prepared by dry agitation. As seen in this figure, the samples prepared with ethanol demonstrated better run-to-run repeatability, indicating a better uniformity of the mixture. However, both the profoundly sigmoidal shape of the conversion curves and somewhat slower conversion rates of the ethanol mixed blends compared to the rate observed with one of the dry mixed samples, implied that this type of blending may have introduced additional structural factors that are not inherent to the reaction. This possibility was further supported by Figure 4.13, comparing the SEM pictures of the products obtained from the dry and wet mixed blends and indicating a significant loss of micro-porosity for the product which originated from the wet blended sample.
Figure 4.12. Effect of mixing method on the temporal conversion of 50 wt% Zn (Sigma-Aldrich)-ZnO (Alfa) blends reacted at 648 K with 15% CO2-Ar. The dashed lines designate experiments that were repeated.
Figure 4.13. SEM pictures of 50 wt% Zn (Sigma-Aldrich)-ZnO (Alfa) prepared by dry (a) and wet mixing (b) after reaction at 648 K with 15% CO₂-Ar.

**Solar-reactor-generated versus commercial Zn-ZnO blend**

The performances of a Zn (Sigma-Aldrich)-ZnO (Grillo) dry mixed blend and the Zn-ZnO powder produced in a solar reactor [28] were compared in Figure 4.14. The samples were of a similar composition (82-85 wt% ZnO). The solar-generated Zn sample reacted ~10 times faster than the commercial blend achieving a slightly lower asymptotic conversion. Although this difference in reactivity is expected based on the measured differences in BET areas (21.98 vs. 1.5 m²/g, Table 4.2), it is uncertain how much Zn alone contributes to the overall solar powder BET area. The morphology of ZnO in the solar powder that is specific
for the solar reactor/quencher operation could be an additional factor contributing to higher reactivity of the solar Zn.

Figure 4.14. Performance comparison between solar Zn-ZnO [28] and Zn (Sigma-Aldrich) /ZnO (Grillo) mixtures having a similar composition: experiments conducted at 623 K with 15% CO₂–Ar.

4.3.3 Discussion

The findings of this study combined with previously reported observations imply that Zn oxidation by CO₂ comprises myriad of physical and chemical steps. In search for a plausible reaction mechanism that is consistent with the available information, a simplified scenario is speculated as described in Figure 4.15. Its key assumption is that the ZnO is being formed through the following mutually competing paths:
(A) Direct Eley-Rideal type reaction [130] or nucleation and lateral growth forming an impervious polycrystalline ZnO scale on the Zn surface. Once the scale growth covers the entire Zn surface, further reaction becomes rather slow as it becomes controlled by the diffusional Zn transport to the outer surface which eventually diminishes at scales as thin as few tens of nm [36, 116]. The impervious ZnO scale may occasionally rupture [44] or spall from the Zn surface due to the thermo-mechanical stresses and structural misfit at the Zn/ZnO interface [131, 132].

(B) Zn vapor transport from the exposed Zn surface to the growing ZnO surface and the diluent ZnO surface followed by the Zn adsorption, activation, and reaction within the ZnO matrix [115].

(C) Fast equilibrium gas-phase reaction between the Zn vapor and CO₂ followed by slower ZnO nucleation & growth and/or precipitation on:
   (I) the ZnO product surface or
   (II) the ZnO (or other) diluent surface.
In light of this scenario, step A results in blockage of the Zn surface by the impervious product scale hence it has an adverse effect on the asymptotic conversion of Zn. Steps B and C produce ZnO outside Zn particles thus they are detrimental to the asymptotic conversion only if the product ZnO plugs the pores between the particles due to its higher molar volume as compared to Zn \([121]\). The experimental observations relative to the asymptotic conversion of Zn discussed in previous sections are reconciled with the previously reported findings as follows.

1. **Effect of mass fraction of inert solids.** The presence of solid ZnO diluent increases the asymptotic conversion by any combination of the following effects:
   a. it favors steps B and C, thereby delaying the blockage of the Zn surface (see Figure 4.16),
   b. it suppresses pore blockage by swollen particles \([121]\) or spalled product scale, and

\[
\begin{align*}
\text{Zn}_{(s)} & \leftrightarrow \text{Zn}_{(g)} + \text{ZnO}_{(s)} + \text{CO}_{(g)} \\
\text{ZnO}_{(s)} + \text{CO}_{(g)} & \rightarrow \text{Zn}_{(s)} + \text{CO}_{2(g)} \\
\text{ZnO}_{(g)} + \text{CO} & \rightarrow \text{ZnO}_{(s)} + \text{CO}_{2(g)} \\
\end{align*}
\]
Effect of the presence of inert diluents on Zn oxidation

c. it keeps the Zn particles apart, thereby hindering their sintering into larger agglomerates that react considerably slower than the original particles [133].

2. *Effect of inert particle properties and mixing quality.* The effect of a solid diluent depends not only on its fraction but also on its morphology, homogeneity of its blend with Zn, and chemical compatibility of its surface with either Zn or ZnO. The poor performance of the Al₂O₃ compared to three ZnO diluents as illustrated in Figure 4.11 could be attributed to any of these factors. In addition to its markedly different morphology compared to ZnO particles (Figure 4.5), the Al₂O₃ material was free-flowing and had a tendency to segregate from Zn particles during blending. Imperfect mixing and blend heterogeneity resulting from it could also explain why wet-blended Zn-ZnO mixtures demonstrated better run-to-run reproducibility than dry-mixed ones did (Figure 4.12 versus Figure 4.8 and Figure 4.11).

3. *Effect of CO₂ concentration.* An increase in CO₂ concentration facilitates nucleation of the ZnO which leads to a faster coverage of the Zn surface by the product scale [44]. In addition, the polycrystalline product scale becomes finer containing less defects [44] which increases its resistance to spalling as well as the tendency of spalled scale to sinter around the Zn surface [131]. All of this is reflected by a lower asymptotic conversion. Adding a ZnO diluent provides an extra surface which competes for the reaction sites with the Zn surface thus maintains unimpeded exposure of Zn vapor to CO₂, suppresses the adverse effect of CO₂ concentration on the asymptotic conversion (Figure 4.10) by providing an extra surface which competes for CO₂ and reaction sites with the Zn surface allowing unimpeded supply of Zn vapor over a longer reaction time (Figure 4.16). An increase in reaction temperature facilitates paths B and C via (i) a higher vapor pressure of Zn and (ii) intermittent rupture of the impervious ZnO scale due to
stresses imposed by the Zn vapor pressure buildup underneath [44]. The latter not only exposes fresh Zn but it also has an autocatalytic effect on steps B and C by creating a fresh ZnO surface. Consequently, the effect of a solid diluent is not as pronounced at higher as it is at lower temperatures.

Figure 4.16. Effect of reaction paths B and C on blockage of the Zn surface in the absence (a) and the presence of solid diluent (b) as an extension of the mechanism proposed in [44].

### 4.4 Summary and Conclusions

This work examines the effect of dilution with inert particles on the Zn oxidation by CO₂. It has been motivated by the fact that the fraction of ZnO in a mixture with Zn leaving the solar thermolysis step generally varies with a solar reactor/quencher design and experimental conditions.
Commercially available particles were used to prepare Zn-ZnO and Zn-Al₂O₃ blends that were tested in a TG setup free of heat and mass-transfer intrusion using a 15% CO₂ - Ar mixture or pure CO₂ at 623 K<T< 673 K and ambient pressure. The presence of a ZnO diluent generally increased the asymptotic conversion of Zn and made it less affected by the CO₂ concentration in gas phase. The presence of Al₂O₃, however, showed no positive effect on the asymptotic conversion. The effect of a solid ZnO diluent was more pronounced at lower than at higher temperatures. At 673 K, ~95% of Zn was converted to the product after being diluted with 50 wt% ZnO, resembling the composition of a typical product mixture generated in a solar reactor. This particular finding implies that reacting Zn above its boiling point is not the only path towards improved utilization of Zn for fuel production. Both the reaction rate and repeatability of the experiments were greatly influenced by the method used to mix Zn and inert powders. The above observations combined with findings from previous studies were used to hypothesize a simplified multi-path reaction mechanism. The results imply that a kinetic model to be used for scale-up and efficiency optimization of the Zn-ZnO thermochemical cycle should not be based on investigating surrogate materials without understanding their relevance to the material they are intended to resemble. In the next step, similar studies with well-characterized Zn-ZnO blends are to be extended to oxidations by H₂O and H₂O+CO₂.
5 Conclusions and outlook

5.1 Conclusions

Two-step solar- thermochemical cycles for reducing mixtures of CO₂ and H₂O into high quality synthetic gas (syngas) using Zn/ZnO and FeO/Fe₃O₄ redox reactions were considered. Advancements were made towards the fabrication of an efficient reactor to carry out the low temperature step of the cycle.

5.1.1 Thermodynamic and kinetic evaluation of H₂O/CO₂ reduction with Zn or FeO

Zn/ZnO and FeO/Fe₃O₄ were recognized as promising candidates to carry out the H₂O/CO₂ splitting solar thermochemical cycle. The feasibility of syngas production with both Zn and FeO was proven thermodynamically and experimentally. Thermodynamic equilibrium computations revealed that the formation of C is favored at below 1000 K and high quality syngas can be produced for both systems at above 900 K. The two systems were investigated in dynamic thermogravimetric experiments combined with gas chromatography in the temperature range of 673 - 1173 K for Zn and 923 - 1423 K for FeO. Both solids produced high quality syngas under the temperature ranges investigated and exhibited comparable conversion rates and final reaction extents. A strong dependency between the H₂O/CO₂ molar ratio of the input gases and the H₂/CO molar ratio of the product gases was shown which in an industrial application could be used to tune the produced syngas to the composition readily suitable for further
processing. Contrary to the thermodynamic calculations, no methane or carbon production was observed and only ZnO and Fe$_3$O$_4$ were attained as solid products. The two solid reactants exhibited good potential both in terms of thermodynamics and syngas yields but Zn reacted at lower temperatures and has a higher maximum theoretical solar-to-fuel efficiency and was thereby chosen for further investigation.

5.1.2 Reactor engineering aspects of H$_2$O/CO$_2$ reduction with Zn

An evaluation of the kinetic behavior of CO$_2$ and H$_2$O reduction by Zn was performed in laboratory-scale packed bed reactor. This reactor type was chosen for its ability to provide useful kinetic information with a simple design and low building and operation effort in contrast to more complicated contacting types that involve particle motion. A wide range of H$_2$O/CO$_2$ mixtures were reacted with blends of commercial Zn-ZnO particles containing 33-67 wt% ZnO at $T_i = 678$ K. Both the reaction rate and final reaction extent increased with increasing weight fraction of ZnO present in the solid mixture and high overall Zn conversions of 0.72-0.91 were measured over a range of H$_2$O/CO$_2$ concentrations. The H$_2$/CO ratios of the syngas corresponded to H$_2$O/CO$_2$ ratios in the inlet flows as near complete conversions of the gaseous reactant occurred for the greatest part of the process. The reaction times were below 10 minutes for all samples. Large increases in the bed temperature were observed during the experiments as a result of fast reaction rates and high exothermicity enhancing both local sintering and cracking of the ZnO shell surrounding the Zn particles. Zn-ZnO mixtures produced from solar thermolysis of ZnO were also tested under similar conditions and proved to be highly reactive yielding overall Zn-to-ZnO conversions of ~0.96 without any additional ZnO dilution. The partial re-oxidation of Zn-to-ZnO during the solar Zn production step can therefore readily provide the inert support needed for efficient H$_2$O/CO$_2$ reduction in the second step of the cycle. Overall, the reactive
system in the presence of a sufficient amount of inert solids showed fast apparent reaction rates, high Zn-to-ZnO conversions and good potential for solid product recovery and cyclability as not cohesion of the particles to the reactor was observed. The information acquired from these small scale experiments are to be used for the development of the final reactor design.

5.1.3 Effect of presence of inert diluents on Zn oxidation

The effect of dilution with inert particles on the Zn oxidation by CO₂ was systematically investigated. The study was motivated (i) by the positive effect of the addition of ZnO diluent on the kinetics of Zn oxidation observed in literature and in the packed bed reactor experiments of Chapter 3 and (ii) by the fact that the fraction of ZnO in a mixture with Zn leaving the solar thermolysis step generally varies with a solar reactor/quencher design and experimental conditions. The above make this study a crucial step towards the development of a reliable kinetic model able to describe the oxidation of solar Zn that can be used for scale-up and optimization of the cycle efficiency. The latter should be sought as a compromise between a higher fuel yield due to a higher Zn-to-ZnO conversion and the energy penalty imposed by a lower ZnO-to-Zn conversion in the solar thermolysis reactor. Commercially available particles were used to prepare Zn-ZnO and Zn-Al₂O₃ blends that were tested in a TG setup free of heat and mass-transfer intrusion using a 15 %CO₂ - Ar mixture or pure CO₂ at 623 K < T < 673 K at ambient pressure. The effects of diluent type, mass fraction, and blending method are reported and used to hypothesize a simplified multi-path reaction mechanism. The presence of a ZnO diluent generally increased the asymptotic conversion and made it less affected by the CO₂ concentration in the gas phase. The presence of Al₂O₃ showed no effect on the asymptotic conversion. The results imply that a kinetic model to be used for scale-up of the Zn-ZnO thermochemical cycle
should not be based on investigating surrogate materials without understanding their relevance to the material they are intended to resemble.

5.2 Outlook

5.2.1 Reactor development

The packed bed reactor was adequate for a first assessment of the reactive system in laboratory scale experiments but would be unsuitable for industrial application due to excessive pressure drops caused by the small particle size, large temperature gradients resulting from the high exothermicity of the reactive system combined with low heat exchange properties and inefficient particle loading and unloading. Further investigation could be performed in the aerosol flow reactor employing lower saturation temperatures to avoid Zn condensation on the reactor walls and increasing the residence time to achieve higher conversion of the Zn particles collected in the filter. However, it is unlikely that the wall depositions could be fully avoided and high Zn-to-ZnO conversions could be reached with this reactor concept. On the other hand, the concept envisioning the oxidation of Zn\textsubscript{(g)} on the walls of a tubular flow reactor is tempting as it offers rapid reaction rates and near-complete Zn-to-ZnO conversions but an efficient method for ZnO recovery from the reactor walls will have to be developed before the reactor is considered for practical applications. The rotary type reactor and the fluidized bed reactor have been recognized as the most promising reactor options. Both of them can operate in the particle size range expected for Zn particles to be produced in the solar reactor and allow for continuous loading/ unloading of the solid particles for transportation and treatment in the solar reactor. The fluidized bed offers additionally good heat exchange properties and possibility of close-to-isothermal operation conditions but faces the challenges of high
particle agglomeration, erosion of equipment, high complexity in the process design and control and low gas conversion due to bubble formation and bypassing. The latter can be dealt with by installing multiple beds in series, internal bubble-breaking structures or recycling the gas to achieve high conversions. On the other hand the rotary cylinder reactor doesn’t face the issues of high pressure drops and particle agglomeration and allows for efficient gas-solid contacting but suffers from poor heat transfer characteristics which make heat exchange and recovery hard and give rise to large temperature gradients. It is important to note that, before the reactor design is finalized, the morphology and reactive behavior of the feeding particles have to be well understood and characterized. However, the solar reactor that will produce the particles is still under development and the final characteristics of the particles are unknown complicating the development of the reactor design. Once the reactor choice is made, a laboratory-scale reactor should be built and tested. Subsequently, a reactor model should be developed coupling heat and mass transfer with reaction kinetics. Finally, system integration studies should be performed.

5.2.2 Kinetic analysis of the effect of inert diluent on Zn oxidation

The effect of inert dilution on the oxidation of Zn should be investigated further as its understanding will be a crucial step towards the development of a kinetic model to be used for the reactor design. If the research continues with powder blends, a more effective mixing method should be developed and more thorough solid characterization should be performed to enable the correlation of the particle morphology to the reaction kinetics and eventually the development of a rate law that can predict the kinetics of particles with the complex solar Zn morphology. Alternatively, in a less fundamental but also less complex approach, a phenomenological rate law could be developed
using Zn/ZnO powders produced in a laboratory-scale solar reactor under versatile experimental conditions to cover a large range of possible properties (particle morphology, ZnO content) which could be encountered in the final product of the solar reactor. Eventually, a rate law for CO$_2$ splitting with Zn should be developed as a function of temperature, gaseous reactant and product concentration, time as well as solid-diluent size, morphology, mass fraction and blending with solid reactant. Finally, similar studies with well-characterized Zn-ZnO blends are to be extended to oxidations by H$_2$O and by concurrent H$_2$O and CO$_2$. 
Appendix A. Evaluation of setups for kinetic analysis

The extraction of reliable kinetic information from experiments involving gas solid reactions requires an adequate setup, able to measure the “intrinsic” kinetics for a given particle source as a function of temperature, reactant and product concentration in the gas phase and temporal conversion/available surface area. In this section, three thermogravimetric setups are evaluated regarding their ability to measure reaction rates, free of heat and mass transfer intrusion. Two Zn-ZnO samples coming from different sources are examined in the setup which exhibited the highest performance. The maximum reaction rate which allows non-intruded measurements is determined. This investigation corroborates the reliability of the kinetic information presented in Chapters 2 and 4.

A.1. Introduction

It has been well documented that experimental conditions such as heating rate, sample mass, gas flow rate and/or pattern, and crucible shape can all have a significant influence on the apparent gas-solid reaction kinetics extracted from a set of TG experiments [134, 135]. The physical transport limitations that are typically encountered are in: (a) external film diffusion heat and mass transfer from the bulk gas to the

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exterior of the sample contained in the crucible, and/or (b) internal heat and mass transfer within the bulk sample bed. The transport effect within an individual particle is generally not considered an experimental artifact. Instead, it is either (i) lumped into the overall kinetics and tied to a specific particle size of interest or (ii) it is extracted from intrinsic kinetics after investigating a range of particle sizes. Therefore, ensuring measurements of the Zn oxidation kinetics free of the heat and mass transfer intrusion warranted an evaluation of different experimental TG setups as an essential step of the experimental program.

A.2. Experimental part

A.2.1. Setup

Figure A-1 illustrates three flow configurations in two furnaces (Netzsch 409CD and 409STA) that have been available for this study. In configuration 1 (409CD, Figure A-1 a), the mass balance purge Ar flow ($V_{Ar,0}$) was pre-mixed with pure CO$_2$ at the bottom and then the resulting gas mixture flew past the crucible to leave the furnace through the exit port positioned at the top. Although in a different furnace (409STA), configuration 2 (Figure A-1b) was essentially the same except that the reacted gas mixture exited through the port installed at the bottom of the furnace, thereby causing a different flow pattern around the crucible. Finally, configuration 3 (also 409STA, Figure A-1c) attempted to provide a more intimate contact between the reactants by introducing the reacting gas mixture through the top of the furnace separately from the balance purge Ar flow which was still flowing from the bottom. While the balance Ar purge flow was a constituent of a reacting CO$_2$-Ar mixture in configurations 1 and 2, it was assumed that in configuration 3 it mixed with a CO$_2$-Ar feed flowing from the top only after the latter has already left the reaction zone. Therefore, the
balance purge Ar flow rate was not included in setting a CO$_2$ concentration and total gas flow rate for experiments in configuration 3.

Figure A-1. Schematic of different gas flow configurations evaluated for the heat and mass transfer intrusion in two furnaces: Netzsch 409CD (a) and Netzsch 409STA (b, c).
The performances of three configurations schematically represented in Figure A-1 were compared by reacting particle mixtures containing 50 wt% Zn (Sigma-Aldrich, 98+%) and 50 wt% ZnO (Grillo) with 15% CO₂ (Pangas 4.5, ≥ 99.995%), in Ar (PanGas, purity 99.999 %) at 723 K. The reaction temperature was chosen to ensure a high reaction rate thus exaggerate physical transport effects. In all cases, prior to heat-up, the chamber was flashed with Argon until the level of O₂ was below 300 ppm to avoid the oxidation of Zn with O₂ before the beginning of the experiment. The chamber was subsequently, heated in Ar at a rate of 10 K/min to the desired temperature. Once the temperature was stabilized, the CO₂-Ar mixture was introduced into the chamber. The total volumetric flow rate, $\dot{V}_{\text{total}}$, was set to 152 mlN/min unless reported otherwise. The configuration 3 was tested with two balance purge Ar flow rates in order to check whether the purge flow affected the effective CO₂ concentration during the reaction. The configuration which exhibited the best performance was further evaluated for the sample mass effect for both commercial Zn-ZnO blends and solar Zn produced in the solar reactor described in [28, 105].

A.2.2. Results and discussion

Configuration evaluation

The conversion-versus-time curves recorded during the setup evaluation with commercial Zn-ZnO blends are shown in Figure A-2. Their general initial sigmoidal shape has been attributed to establishing a setpoint CO₂ concentration after a step change from Ar to a CO₂-Ar feed at the beginning of an experiment. The slight differences in the asymptotic conversions observed in this figure cannot be explained; this, however, did not hinder further evaluation of the setups. Good agreement of the results obtained with different balance purge flow rates in configuration 3 (Figure A-2b) confirmed the hypothesis that the mass balance Ar purge stream introduced from the bottom did not reach the
reaction zone. The slower conversion rates observed in configurations 1 and 2 (Figure A-2a) indicated that these were certainly intruded by transport effects.

A time independent rate of a gas-solid reaction reflected by a linear conversion-versus-time relationship coupled with its weak temperature dependence is a typical sign of the film diffusion mass transfer limitation [133]. Therefore, the remarkable linearity of the major parts of the plots that in Figure A-2a refer to configurations 1 and 2 implied that these experiments were potentially intruded by the CO₂ transfer from the bulk gas to the crucible. Effect of the film diffusion resistance around individual particles within the samples was ruled out because it could not have been related to the macro-flow pattern within the furnace.

In order to confirm the culprit for the observed performance discrepancy among the configurations tested, the effects of sample mass (50 and 87 mg) and total CO₂-Ar flow rate to the sample (100 and 165 mlN/min) were explored in configuration 1 with 50 wt% Zn (Sigma-Aldrich)-ZnO (Grillo) samples in 15% CO₂ at 723 K. Recorded temporal sample mass gains that reflect the effective temporal oxygen uptake are presented in Figure A-3. They indicate that the oxygen uptake did not depend on either time or sample mass but it increased with an increase in the total flow rate. This evidence is consistent with the hypothesis that the mass transfer of CO₂ from the bulk gas to the crucible controlled the oxidation rate in configuration 1.
Figure A-2. Zn conversion curves for reaction of 50% Zn (Sigma-Aldrich) - ZnO (Grillo) at 723 K with 15% CO$_2$- Ar performed (a) in the three flow configurations illustrated in Figure A-1 and (b) in configuration 3 with two balance purge flow rates.
Determination of limiting experimental conditions for a specific configuration

Conversion determined from a TG experiment that is independent of sample mass rules out a possible intrusion by either external or internal transport effects. Therefore, since configuration 3 measured the fastest reaction kinetics it was further evaluated for the sample mass effect. In Figure A-4 an example is shown where the set of parameters permits non-intruded measurements for 67% ZnO (Grillo)-Zn (Sigma-Aldrich) with 15% CO₂ at 673 K. Since the conversions resulting from the two sample masses show good agreement, the CO₂ concentration, temperature, and the higher sample mass employed in these experiments were considered to represent the maximum values that should be used for adequate assessment of the oxidation kinetics with this particular blend.
It should be noted that the limiting experimental conditions determined in the mass independence study of Figure A-4 are not global for this setup but sample-specific and depend on the reactivity of the active solid. As an example, the results of reaction of a more reactive solar Zn-ZnO mixture are demonstrated in Figure A-5 in experimental conditions that matched the ones applied the sample shown in Figure A-4. Even though the same temperature, CO$_2$ concentration and $\dot{V}_{\text{total}}$ were used the sample showed a mass independent oxygen uptake indicating intruded measurements. As an additional proof of the intrusion, repetition of the experiment at a the lower temperature of 648 K was conducted and demonstrated that the oxygen uptake remains unchanged with temperature and thereby the limiting mechanism is the temperature independent gas diffusion from the bulk to the crucible rather than the temperature dependent chemical reaction.
Figure A-5. Temporal sample mass gain as function of sample mass and reaction temperature: TG configuration 3, solar Zn (81 wt% ZnO-Zn) with 15% CO₂-Ar.

For the oxidation of highly reactive solar samples with 15% CO₂, the temperature had to be decreased to 623 K and the sample mass to 30 mg for non-intruded measurements to be obtained as seen in Figure A-6 for solar Zn containing 70.8 wt% ZnO.

Overall, the maximum CO₂ consumption rate measured in a non-intruded experiment was 0.12 mmol/min and can be used as a faster alternative to a mass independence study for the evaluation of the upper limit of experimental conditions permitted for a specific sample in configuration 3 under $\dot{V}_{total} = 152 \text{ ml}_N/\text{min}$. 
A.3. Summary and conclusions

Three thermogravimetric setups were evaluated regarding their ability to measure “intrinsic” reaction rates, free of heat and mass transfer intrusion. Mass and flow independency studies showed that mass transfer of CO$_2$ from the bulk gas to the crucible controlled the oxidation rate for the two worst-performing setups under the experimental parameters tested for a commercial blend containing 50 wt% ZnO. Further testing of the configuration which measured the fastest reaction kinetics revealed that non-intruded measurements could be attained only for a limited, sample-specific range of experimental parameters. More specifically, the upper limit for samples containing 67% ZnO (Grillo)-Zn (Sigma-Aldrich) was set to 15% CO$_2$-Ar at 673 K and $m_{s,i} = 55$ mg and for more reactive solar Zn samples containing 70.8 wt% ZnO-Zn to 15% CO$_2$-Ar at 623 K and $m_{s,i} = 30$ mg. The maximum
measured consumption rate of gaseous oxidant which allowed intrusion-free measurements was 0.12 mmol/min for $\dot{V}_{\text{total}} = 152 \text{ ml}/\text{min}$. The setup can be therefore used safely for characterization of reactions consuming gas at rates lower than this critical value when the same total flow rate of gaseous reactant is supplied. This setup was used as a tool to measure kinetic properties during the oxidation of pure Zn and Zn-ZnO mixtures in the studies presented in Chapters 2 and 4.

This section highlights the importance of evaluating the kinetic setups for heat and mass transfer limitations prior to kinetic studies in order to ensure the measurement of intrinsic reaction rates rather than experimental artifacts.
List of figures

Figure 1.1. Scheme of two step H₂O/CO₂- splitting solar thermochemical cycle for syngas production with metal oxide redox reactions.................................................................6

Figure 1.2. Typical model flow diagram of a two-step solar thermochemical cycle for CO₂ splitting applied for the second-law analysis. (taken from [17])...................................................7

Figure 2.1. Equilibrium composition of the gaseous products and solid carbon versus temperature at 1 bar for the systems: a) 2Zn+H₂O+CO₂, b) 3Zn + H₂O+CO₂, c) 6FeO+H₂O+CO₂, and d) 9FeO+H₂O+CO₂...................................................................20

Figure 2.2. Equilibrium compositions of the metal containing solid species versus temperature at 1 bar for the systems: a) 2Zn+H₂O+CO₂, b) 3Zn + H₂O+CO₂, c) 6FeO+H₂O+CO₂, and d) 9FeO+H₂O+CO₂..................................................................21

Figure 2.3. Enthalpy change of the reactions as a function of temperature for the chemical systems: a) 2Zn+H₂O+CO₂ and 3Zn+H₂O+CO₂ and b) 6FeO+H₂O+CO₂ and 9FeO+H₂O+CO₂ assuming reactants at 298 K and products at equilibrium at the given temperature. .................................................................22

Figure 2.4. Reaction extent as a function of temperature at 0.1, 1 and 10 bar, for the systems 2Zn+H₂O+CO₂ (a-b) and 6FeO+H₂O+CO₂ (c-d). .................................................................24

Figure 2.5. Thermogravimetric experimental setup........................................26

Figure 2.6. Reaction extents (solid lines) and temperature (dashed lines) versus time for dynamic TG runs performed with a) CO₂-H₂O/Zn and b) CO₂-H₂O/FeO at various gaseous reactant concentrations.................................................................28
Figure 2.8. Reaction extents (solid lines) and the accumulated normalized amounts of CO (squares), H₂ (circles), and H₂+CO (diamonds) versus time for: a) CO₂-H₂O/Zn system; and b) CO₂-H₂O/FeO system. The molar flow fractions of the gas is $\alpha = 0.2$.

Figure 2.9. Product molar ratio $\gamma$ as a function of reactive gas molar ratio $\alpha$ for the CO₂-H₂O/Zn (circles) and CO₂-H₂O/FeO (squares) systems.

Figure 3.1. Common reactor types used for gas-solid reactions.

Figure 3.2. Representative scheme of aerosol flow reactor for H₂O or CO₂ splitting with Zn (based on [45]).

Figure 3.3. Scheme of packed-bed reactor setup.

Figure 3.4. SEM picture of (a) 50 wt % ZnO mixture prepared with commercial particles, and (b) 75 wt % ZnO mixture obtained by solar thermolysis of ZnO.

Figure 3.5. Inlet (dashed) and outlet (solid) temperatures and molar flow rates of CO (circles) and H₂ (squares) as functions of time for representative experimental runs with (a) a 9,000 mg sample of commercial blend containing 50 wt% ZnO exposed to 300 mlN/min of 50% H₂O–CO₂, and (b) a 6,000 mg sample of solar powder containing 75 wt% ZnO exposed to 80 mlN/min of 50% H₂O-CO₂. The markers represent the GC measurements and the lines the fit of the MS data.

Figure 3.6. Effect of ZnO on temporal Zn conversion for 50% H₂O-CO₂ and sample sizes of 9,000 and 3,000 mg.

Figure 3.7. Temporal conversions of Zn for 50 wt% ZnO with 25, 50, 75% H₂O-CO₂ and 100% CO₂.

Figure 3.8. Individual mean Zn conversions as a function of the % H₂O–CO₂ for commercial 50 wt% ZnO, with sample sizes of 9,000 mg (circles) and 3,000 mg (diamonds), and for solar 75 wt% ZnO (squares) with sample sizes of 6,000 mg. Indicated are the error bars based on individual 95% confidence limits.
Figure 3.9. SEM of products collected from the centre of the bed after reaction with 50% H$_2$O-CO$_2$ for (a) commercial 50 wt % ZnO, and (b) solar 75 wt % ZnO. .................................................................55

Figure 3.10. SEM of products collected from the centre of the bed after reaction with 50% H$_2$O-CO$_2$ for (a) 33 wt % ZnO, and (b) 67 wt % ZnO. ..................................................................................... 56

Figure 4.1. Schematic depicting the stages of Zn oxidation with CO$_2$ comprising (a) initial Zn particle exposed to CO$_2$, (b) interface-controlled reaction, (c) diffusion-controlled reaction and (d) development of cracks followed by interface-controlled reaction of Zn(g) and CO$_2$ [44]........................................................................64

Figure 4.2. Particle-pellet model in case of no added inert particles (left) and in case with added inert particles (right) [121]. .................71

Figure 4.3. Volume-based particle size distributions of raw Sigma Aldrich Zn, Solar Zn, and four inert diluents used in this study: three ZnO materials and one Al$_2$O$_3$..............................................75

Figure 4.4. SEM pictures of (a), (b) Sigma-Aldrich Zn particles and (c), (d) solar Zn particles produced in the solar reactor as described in [28]. ......................................................................................76

Figure 4.5. SEM pictures of (a) Al$_2$O$_3$ particles and ZnO particles purchased from (b) Alfa, (c) Grillo and (d) Fluka. ....................77

Figure 4.6. Effect of the ZnO (Grillo) dilution on the Zn (Sigma-Aldrich) conversion: samples prepared by dry mixing and reacted with 15% CO$_2$ – Ar at 623 K. The dashed lines designate repeated experiments. .................................................................79

Figure 4.7. SEM pictures of Zn (Sigma-Aldrich) before and after the experiment with 15% CO$_2$-Ar at 623 K and no ZnO added. ....81

Figure 4.8. Effect of temperature on conversion of the Zn (Sigma-Aldrich) diluted with 50 wt% ZnO (Grillo) by dry mixing and reacted with 15% CO$_2$ – Ar. The dashed lines designate repeated experiments.................................................................82
Figure 4.9. SEM pictures of products obtained after experiments at 623 K (a) and 673 K (b) described in Figure 4.8................................. 83

Figure 4.10. Effect of CO$_2$ concentration on conversion of the Zn (Sigma-Aldrich) diluted with 50 wt% ZnO (Grillo) by dry mixing and reacted at 648 K. The dashed lines designate repeated experiments................................................................. 84

Figure 4.11. Effect of inert diluent source on the conversion of Zn (Sigma-Aldrich) diluted to 50 wt% by dry mixing and reacted with 15% CO$_2$ – Ar at 648 K. The dashed lines designate repeated experiments............................................................... 85

Figure 4.12. Effect of mixing method on the temporal conversion of 50 wt% Zn (Sigma-Aldrich)-ZnO (Alfa) blends reacted at 648 K with 15% CO$_2$-Ar. The dashed lines designate experiments that were repeated................................................................. 87

Figure 4.13. SEM pictures of 50 wt% Zn (Sigma-Aldrich)-ZnO (Alfa) prepared by dry (a) and wet mixing (b) after reaction at 648 K with 15% CO$_2$-Ar. ................................................................. 88

Figure 4.14. Performance comparison between solar Zn-ZnO [28] and Zn (Sigma-Aldrich) /ZnO (Grillo) mixtures having a similar composition: experiments conducted at 623 K with 15% CO$_2$–Ar................................................................. 89

Figure 4.15. Speculated reaction mechanism. .............................................. 91

Figure 4.16. Effect of reaction paths B and C on blockage of the Zn surface in the absence (a) and the presence of solid diluent (b) as an extension of the mechanism proposed in [44]............... 93

Figure A-1. Schematic of different gas flow configurations evaluated for the heat and mass transfer intrusion in two furnaces: Netzsch 409CD (a) and Netzsch 409STA (b, c)................................................. 103

Figure A-2. Zn conversion curves for reaction of 50% Zn (Sigma-Aldrich) - ZnO (Grillo) at 723 K with 15% CO$_2$- Ar performed (a) in the three flow configurations illustrated in Figure A-1 and (b) in configuration 3 with two balance purge flow rates...... 106
Figure A-3. Temporal sample mass gain as function of sample mass and total gas flow rate to the furnace: TG configuration 1, 50 wt% ZnO (Grillo)-Zn (Sigma-Aldrich) with 15% CO₂ at 723 K...107

Figure A-4. Effect of sample mass on conversion in configuration 3: 67 wt% ZnO (Grillo)-Zn (Sigma-Aldrich) with 15% CO₂-Ar at 673 K..............................................................108

Figure A-5. Temporal sample mass gain as function of sample mass and reaction temperature: TG configuration 3, solar Zn (81 wt% ZnO-Zn) with 15% CO₂-Ar. .................................................................109

Figure A-6. Effect of sample mass on conversion in configuration 3: solar Zn (70.8 wt% ZnO-Zn) with 15% CO₂-Ar at 623 K. ....110
List of tables

Table 1.1. Summary of characteristics of a selection of water-splitting thermochemical cycles. ................................................................. 11
Table 2.1. Properties of Zn and FeO powders used in the TG experiments. ................................................................................................. 27
Table 3.1. Comparison of main gas-solid reactor types (based on tables found in [101, 102] with additional information found in [103]) ........................................................................................................ 38
Table 4.1. Summary of observed effect of T, %CO_2 and %H_2O on final conversion as reported in various Zn-oxidation studies. .......... 68
Table 4.2. Key characteristics of used solid materials.............................. 74
References


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