Iron Oxidation Kinetics for H₂ and CO Production via Chemical Looping

R.C. Stehle, M.M. Bobek, D.W. Hahn

Corresponding Author:

D.W. Hahn
Department of Mechanical and Aerospace Engineering
Box 116300
University of Florida, Gainesville, FL 32611-6300
Telephone: 352-336-1065
Email: dwhahn@ufl.edu

Keywords:

Magnetite; CO Production, Hydrogen Production; Steam-Iron Process; Water Splitting CO₂-splitting

Iron Oxidation Kinetics of H₂ and CO Production via Chemical Looping

R.C. Stehle, M.M. Bobek, D.W. Hahn

Department of Mechanical and Aerospace Engineering, University of Florida,
Gainesville, FL 32611-6300

Abstract

Solar driven production of fuels by means of an intermediate reactive metal for species splitting has provided a practical and potentially efficient pathway for disassociating molecules at significantly lower thermal energies. The fuels of interest are of or derive from the separation of oxygen from H₂O and CO₂ to form hydrogen and carbon monoxide, respectively. The following study focuses on iron oxidation through water and CO₂ splitting to explore the fundamental reaction kinetics and kinetic rates that are relevant to these processes. In order to properly characterize the reactive metal potential and to optimize a scaled-up solar reactor system, a monolith-based laboratory reactor was implemented to investigate reaction temperatures over a range from 990 to 1400 K. The presence of a single, solid monolith as a reacting surface allowed for a limitation in mass transport effects in order to monitor kinetically driven reaction steps. The formation of oxide layers on the iron monoliths followed Cabrera-Mott models for oxidation of metals with kinetic rates being measured using real-time mass spectrometry to calculate kinetic constants and estimate oxide layer thicknesses. Activation energies of 47.3 kJ/mol and 32.8 kJ/mol were found for water-splitting and CO₂ splitting, respectively, and the conclusions of the independent oxidation reactions were applied to experimental results for syngas (H₂-CO) production to explore ideal process characteristics.

Keywords: Magnetite; CO Production, Hydrogen Production; Steam-Iron Process; Water Splitting CO₂-splitting

1. Introduction

1.1 Overview

While the impact CO₂ emissions have on the ecosystems of our planet continues to attract attention, a significant increase in CO₂ emissions resulting from our need to meet the growing energy demands via hydrocarbon fuels are generally assumed to have a non-neutral effect on the environment. Numerous alternative energy sources are being widely studied and tested, but when it comes to effectiveness in creating a new energy infrastructure that would produce the necessary energy density to meet demands, solar technology appears to show strong promise. The sun supplies around 100,000 TW of energy to the earth, which is nearly 7000 times more than our current need [1]. In other words, 1 hour of direct sunlight contains enough energy potential to provide our yearly energy demand. An interesting solar collection technique derives from using the process heat obtained from concentrated solar energy. The process heat can be used to drive chemical reactions in order to store the solar energy as liquid or gaseous fuel. The resultant fuel source could act as a synthetic hydrocarbon that can be utilized in the current infrastructure for electrical and mechanical energy devices. The benefit of the synthetic fuel or solar fuel would be the opportunity to create a carbon neutral economy. The chemical processes that have become most attractive for fuel production originate with CO₂ and H₂O that act as oxidants when introduced to metal alloys that have been reduced to low oxide states by thermally concentrated solar heat. During the species splitting oxidative process, CO₂ and H₂O produce CO and H₂, respectively, after which water gas shift and Fischer-Tropsch processes can be further utilized to obtain the necessary hydrocarbons in liquid form [2-4]. The driving source for the chemical looping steps is the active metal alloy that must be constantly reduced under high thermal temperatures and re-oxidized to reflect a regenerative process [5, 6]. Materials that would oxidize efficiently while maintaining their material integrity have been the subject of recent efforts which have focused on a handful of transition metals [7-9]. Iron oxides and iron ferrites are a popular material under current investigation, and are the main focus of this study [10-12]. The following global chemical reaction of Reactions (1) and (2) represents the overall processes, with Figure 1 detailing the equilibrium thermodynamic predictions.

1.2 Syngas Production

The continued research in storing solar energy as fuel has led to the popular concept of producing syngas with the potential of processing it into liquid hydrocarbon fuels that can be implemented into the current fossil fuel economy. Smestad and Steinfeld reviewed the cost analysis and thermodynamic efficiencies for photochemical and thermochemical fuel production

techniques, and discussed the potential for thermochemical cycles being much more efficient and less costly with the greatest benefit being related to liquid hydrocarbon fuel production for the transportation sector [13]. An additional study done by Loutzenhiser et al has shown through second-law analysis, indications for achieving high solar-to-chemical energy conversion efficiencies that demonstrate economic dominance over the competing solar fuel production techniques [14]. The benefits in combining these two processes as a single step go beyond the positive implications for reactor implementation. There have been experimental studies done on the interactions of water-vapor when exposed to gas mixtures containing CO₂ in the presence of alloys [15]. Kim and his colleagues demonstrated in their study on system analysis for fuel production from splitting both CO₂ and H₂O together definite advantages over splitting the species independently [16]. Through their analysis, process efficiencies would increase in the combined process along with the possibility of increased fuel yields. Loutzenhiser and Steinfeld also highlighted this consideration in their thermodynamic cycle analysis for syngas production with the main focus being on the effects of CO₂ concentrations [17]. Stamatiou, Loutzenhiser and Steinfeld have also illustrated the consistency in reaction dependencies over cycle time for the simultaneous oxidation step with the independent reactions where initially quick surface reactions occur upon exposure followed by a slower ionic-diffusion controlled regime [18, 19]. One aspect that is considered in this study on syngas production is associated with how the competing reaction mechanisms of the individual oxidation processes along with possible side reactions will influence the overall process. The produced syngas molar ratios between H₂:CO₂ has significant interest for efficient Fischer-Tropsch conversion and it is apparent that varying CO₂/H₂O flow ratios will have an effect on production concentrations.

1.3 Kinetics

In order to develop a working model for the two step steam-iron process in an actual solar reactor, accurate rate constants from the reaction kinetics should be considered. This study investigates fundamental reaction kinetics through experimental observation of a laboratory-scale reactor working under controlled oxidation conditions. Identification of reaction mechanisms and pathways is essential in beginning any study into accurate kinetic parameter measurements and is the primary focus in reaction rate mechanisms for this study. The steam-iron process may be represented as a catalysis-like reaction under the Mars-van Krevelen modeling form [20], which invokes a surface redox mechanism to describe rates of oxidation reactions on heterogeneous oxide catalysts [21]. Mars-van Krevelen mechanisms correlate to gas molecules reacting with lattice oxygen of the catalyst to produce oxides. Their model depicts oxygen on the catalyst surface reacting with aromatic compounds to form oxidation products and leaving the catalyst site in a reduced state [22]. The reduced catalyst is then re-oxidized by gas phase oxygen in a separate step which replenishes the lattice oxygen [23, 24]. Based on the Mars van Krevelen definition of their reaction mechanism, the following four-step mechanism for the water splitting oxidation reaction step has been proposed [25]:

In the above equations, V represents vacancies in the lattice structure of the metal surface, and O^- represents atomic oxygen in the lattice of the metal oxide. This proposed mechanism can be backed by an electron spectroscopic study done by Roberts and Wood where they showed evidence of OH^- and O^- species being formed simultaneously during the interaction of water vapor. Their results suggest that the first step of water dissociation would be followed by interactions between surface hydroxyls to form chemisorbed oxygen [26]. Between these two steps, the authors suggest that a discrete chemical phase would exist within the lattice as proposed by the above mentioned mechanism. Among the different types of kinetic models that have been represented for oxidation reaction kinetics, JMAK and Cabrera-Mott models have been referred to most frequently and show the best relation in regards to nucleation growth and potential difference.

Cabrera and Mott publicized their theoretical and experimental work on the theory of the oxidation of metals which focuses on oxide film development and the dependence it has on oxidation kinetics [27]. The Cabrera-Mott model is dependent upon the presence of an electric field within the oxide film due to a contact potential difference between the adsorbed oxygen ions and the metal surface [28]. As oxygen or water is dissociatively adsorbed (i.e. chemisorbed) onto a metal surface, the metal acts as an electron donor and a double charge layer is produced. The oxidation rate is then controlled by the diffusion of oxygen anions into the oxide layer from the surface and the diffusion of metallic cations away from the bulk metal [29, 30]. The resulting oxide formation then generally takes place within the bulk oxide layer. This process is initiated by an extremely rapid oxidation to establish the oxide film and electric field. The initial oxidation process is transient and continues until a critical thickness is achieved ($\sim 100 \text{ \AA}$) where growth slows or nearly stops. When the surface of the oxide is exposed to available atomic oxygen, electrons pass through the oxide from the metal. This movement can be characterized by thermionic emission or tunneling effect mechanisms and should occur much more rapid than ionic motion. The absorbed oxygen atoms would then be converted to O^- ions forming a field across the oxide layer which would be maintained until quasi-equilibrium is achieved [31]. The potential formed across the layer should be independent of oxide layer thickness allowing electrons to pass through the layer until equilibrium is reached.

At the typical reaction temperatures of interest ($\sim 1275 \text{ K}$), the mobility of the oxygen and metallic ions is expected to be very high, hence diffusion limitations are not considered significant except for oxides thickness exceeding several microns, as discussed later. For the

rate-limiting condition of water chemisorption, an effective one-step reaction rate may be expressed in the form:

$$\frac{dH_2}{dt} = k_{eff}[H_2O]^x \quad (7)$$

Hydrogen production is per unit surface area, which is considered as the actual surface area of the reactive metal oxide (i.e. after the initial rapid oxidation of the native reduced metal). The effective rate constant is given by the Arrhenius form below:

$$k_{eff} = Ae^{\frac{E_a}{R}(\frac{1}{T})} \quad (8)$$

with the pre-exponential constant A and activation energy E_a . For the rate limiting step given by water chemisorption, one may consider the activation energy to be consistent with water dissociation on the iron oxide surface. For water splitting in a wüstite/magnetite cycle presented by Charvin et al, it was speculated that hydrogen production rates may be limited by the growing oxide thickness due to steam-transfer [32]. This is consistent with Cabrera-Mott kinetics which state that thermodynamic equilibrium exists at the oxide-metal interface and at the oxide surface resulting in the diffusion of oxygen through the oxide layer under a concentration gradient. This gradient would be inversely proportional to oxide layer thickness and would grow based on parabolic law rate kinetics.

The competing effects of kinetics and diffusion have been noted in other studies as well. Nieves et al. explored steam oxidation for hydrogen production using a ceramic substrate coated with zinc ferrite [33]. They found that the rate-controlling step changes with reaction time, with evidence of internal diffusion through the product playing a role, while further concluding that the reaction is controlled by the chemical reaction initiating the water splitting before the formation of a continuous product layer. An Arrhenius expression was found to describe the temperature dependency of the peak reaction rate. Svoboda and co-workers examined hydrogen production for reduced iron and steam based on thermodynamic equilibrium [34, 35]. From 600 to 800 K, they reported an overall conversion to magnetite with 94.8 to 80% hydrogen conversion rates, respectively. For moderately low temperatures, they suggest that the steam reaction is limited by kinetics. The following study continues the investigation into effective reaction kinetics for the oxidation reaction step of the both the steam iron process and CO₂-splitting process for kinetic constant calculation and reaction mechanism identification via a monolithic surface, thereby uncoupling the effects of heat and mass transport in typical porous bed structures or other non-prescribed surface geometries.

2. Experimental

2.1 Thermal Reactor Concept and Design

A Sentro Tech STT-1700C high temperature vertical tube furnace coupled with a Sentro Tech STT-1200C high temperature horizontal furnace represent the main components of the high temperature reactor. The vertical furnace has an operating maximum temperature of 1973 K with an optimum operating temperature of 1773 K for extended use. This furnace is sufficient for both oxidation and reduction conditions as the main reactor housing. The horizontal furnace is used as a preheater for inert gases and as the heating source for steam generation during oxidation. Just as in the previously reported low temperature furnace, the objective of the design was to construct and instrument a laboratory-scaled reactor to measure fundamental chemical kinetic rates and process efficiency for the oxidation of iron [36]. This design also was intended for oxidation conditions with supplied CO₂ along with conditions for a flow of both steam and CO₂ simultaneously. Also staying consistent with the low temperature furnace, the high temperature reactor was designed to carefully control the flow rates of water and bulk gases, the temperature of the reactor, and the surface area of the reactant metal. The monolith reactor design was implemented for parameter control and to represent a steady state reaction condition. The reactor components are made up of a steam generator, main reactor core, and a post-reaction exhaust heater. The pre-heater section represents the initial length of the 1973 K furnace heating zone because only 25.4 cm of the 45.7 are utilized for reaction length. The other 20.3 cm are used to increase the temperature of the gas mixture just before contact with the iron surface. An additional length between both furnaces has been added in order to properly transition the flow through the pre-heating furnace, into the main reactor. This length is heated with heating tape at 573 K and is insulated efficiently to maintain thermal stability throughout the length. Figure 2 represents the system layout for the oxidation experiment during syngas production under simultaneous CO₂ and water splitting. Liquid water is supplied to the system by means of a syringe pump (BASi) that is passed through a 1.59-mm I.D. stainless steel tube. The tube continues into the horizontal furnace set at 1273 K where liquid water is vaporized to steam. The tube opens up into a 12.7-mm I.D. Inconel 720 tube while still within the heating zone of the horizontal furnace and is then introduced to a flow of a preheated CO₂ and an inert gas mixture of helium and argon. The CO₂ and inert gases are supplied to the system by mass flow controllers. The steam-gas mixture continues through the connecting section between the furnaces, which is a 12.7-mm I.D. stainless steel tube that is heated at 573 K. The steam-gas mixture temperature may decrease slightly during this transition between furnaces but the impact should be limited. The mixture enters another 12.7-mm I.D. Inconel 720 tube within the vertical furnace and will travel 20.3 cm at reactor temperatures before coming into contact with the iron surface.

The iron monolith support is shown in Figure 3. A 0.16 cm stainless steel support is wrapped around the iron monolith, and the assembly is then suspended within the Inconel tube and positioned 25.4 cm into the vertical furnace heating zone. The back end of the stainless steel support is held in place and sealed by Swagelok fittings. The steam-gas mixture will pass over the hanging iron and react with the surface to produce a H₂, CO and a resultant oxide layer. The produced gases along with the supplied inert gases and left over steam and CO₂ will exit the

furnace. The exhaust species pass through the same heated exhaust section from the low temperature reactor that acts as a thermal buffer downstream before the gases leave the system.

2.2 Data Acquisition System

At the exit of the reactor section a heated quartz capillary tube is inserted to sample and transport the product gases to a mass spectrometer for real-time analysis (16 cc/min sample rate). The electron-ionization quadrupole mass spectrometer (Hiden model HPR-20) was used for select ion monitoring, and the operating emission was set at 40 μ A with a multiplier setting of 900 V. The resultant real-time, mass-to-charge ratios of each species are recorded to produce the resulting volumetric flow rates per unit area with the analytical measurement of produced species being obtained from the signal ratio of the produced species to that of a known volumetric flow rate of an inert gas. Calibration curves were developed for mass-to-charge ratios of H_2/Ar , H_2/He , CO/Ar and CO/He for a broad range of controlled flow rate ratios. The calibration data was obtained by flowing hydrogen or CO, helium and argon through the thermal reactor at known flow rates. The reactor temperature during these tests was 1073 K and each data point was recorded by averaging the resultant signal over 2 minutes. Calibration between the inert gases was also done for internal data acquisition consistency. Before each experiment, the signal ratios measured by the mass spectrometer were checked for appropriate relation based on the calibration data at the set flow rates. This would help prevent system error during experimental tests and to ensure no mass spectrometer component failure. The calibration constants obtained were checked for accuracy periodically to ensure no changes between the relative signals measured from the mass spectrometer occurred and represent the relative sensitivity of the mass spec system between any two species.

Additional calibration is needed to take into account the signal response due to the fragmentation or fractionation of water into hydrogen ions, and CO_2 into CO within the mass spectrometer. During the ionization process, species generally fractionate into compounds due to the high ionization energies associated with the process. Because water will fractionate readily into H and OH, creating H_2 in the process, the recorded H_2 signal needs to be corrected for the additional signal of hydrogen originating from actual H_2O . This was done by obtaining a fractionation constant between the signal of water and hydrogen for a flow containing only inert gas and steam under non-reacting conditions (i.e. no iron rod present). The calculated fractionation constant (~4%), was then used to determine the amount of fractionated H_2 corresponding to the amount of detected water, which was then subtracted from the total H_2 signal. In practice, the contribution of the hydrogen signal from fractionated water ranged from about 5-10% for the investigated temperature range and the contribution of the CO signal from fractionated CO_2 ranged from 40% of total CO signal at 1373 K to nearly 90% for production done at 973 K.

2.3 Experimental Procedure

A temperature range of 973 to 1473 K was investigated for two sets of oxidation processes with the first being the steam-iron process. The flow rates for the inert gases were kept constant for all experimental tests with argon at 200 mL/min and helium at 100 mL/min. Liquid water was supplied at 12.5 μ L/min initially and was altered throughout each experimental run between 12.5 μ L/min, 25 μ L/min and 50 μ L/min for concentration dependence data. Six experiments were done at each of five temperatures within the investigated temperature range: 973, 1073, 1173, 1273 and 1373 K. For each operating temperature, the experiments were performed under oxidation conditions for 1 hour. Prior to each experiment, a pristine iron rod was polished using a successive series of grit papers, namely 320, 600 and finally 1200, and then carefully cleaned with acetone to produce a polished rod free of any surface oxidation. This procedure was done just prior to insertion of the rods into the room temperature reactor. Inert gas flow was then established, and the reactor was then heated to the desired operating temperature. Once the steady-state reactor conditions were realized, a process that generally required in excess of 1 hour, the mass spectrometer was initiated and the experiments were started by initiating the flow of water through the syringe pump. An initial transient in the species concentrations was observed that lasted for only several minutes, after which steady-state conditions were realized as discussed below.

The mass spectrometer recorded the signals of hydrogen, helium, argon, and water with a temporal resolution of about 4.6 s, and the resultant signals are tabulated for further data analysis. The water flow rate was increased to 25 mL/min after 20 minutes and increased again to 50 mL/min at the 30 minute mark. The flow rate was lowered back to 25 mL/min and then 12.5 mL/min in 10 minute increments. After 1 hour, the water flow was stopped and the entire reactor was cooled back to room temperature under the flow of inert gas only. The iron rod was then removed from the reactor and immediately stored under inert gas for future investigation into chemical phase and oxide layer thickness using Raman spectroscopy, electron dispersive spectroscopy (EDS), and high resolution SEM analysis.

This experimental process was reiterated again for CO production under the flow of CO₂ for temperatures of 1073, 1173, 1273, 1373 and 1473 K under the same inert gas flow conditions. Table 1 lists the gas and water flow rates that were used during experimentation, with all gas volumetric flow rates corresponding to a state of 298 K and 1 atm pressure.

3. Results and Discussion

3.1 Hydrogen Production Analysis

The previous study into the oxidation of iron for hydrogen production for reactor temperatures between 600-850 K resulted in the identification of possible reaction pathways during the oxidation step in reference to the Cabrera-Mott model for the oxidation of metals [36]. This result was partially based on analysis into the oxide morphology post reaction which determined the state of the oxide on the surface of the monolith structure to be nearly entirely magnetite with an iron to oxygen gradient being present throughout the oxide layer that

decreased from the oxide surface to the iron-iron oxide interface. This observation promoted the possibility of iron cations diffusing away from the bulk material into the oxide and oxygen ions from the surface moving into the oxide layer where oxide formation would generally occur within the oxide layer. A multistep mechanism was proposed and reevaluated in the form seen below where V corresponds to oxygen vacancies in the lattice structure of the metal surface.

Reaction 9 corresponds to a global reaction in which hydrogen and chemisorbed oxygen are formed from the dissociation adsorbed water vapor. The activation energy reported by the study from the investigation of first order reaction kinetics was estimated to be on the order of 50 kJ/mol which is consistent with water decomposition energies. From this understanding, the water chemisorption step of Reaction 9 was identified as the possible rate limiting step for the oxidation reaction process.

The kinetic investigation for the low temperature (670-875 K) water-splitting experiments utilized a first order approximation for the water chemisorption step to determine kinetic parameters. This approximation was supported by the assumption that at low temperatures the oxidation step is limited by kinetics and that a lack of dependence on water transfer to the surface would exist. In preparation for the new investigation into higher reactor temperatures, the first order approximation was tested by oxidizing iron species at 850 K under the presence steam at different flow rates to represent water concentration values from 1-15%. The volumetric production rates of hydrogen with respect to water concentration from experiment are plotted in Figure 4 which show a linear increase in production as concentration increases up to about 8%, where there after the curve begins to smooth out to resemble no further effect on water concentration. The result for concentrations above 8% is consistent with the reported findings of Neises et al where a negligible dependence on water concentration in the range of 10-80% would exist. For concentrations below 8%, which correspond to the study done here, The Van Hoff plot in Figure 4 shows the reaction order to be $\sim 1/2$. This finding does not have major implications on the reported kinetic parameters; however it does give further support for the proposed Cabrera-Mott mechanism during species chemisorption. An interpretation of dissociative adsorption by Langmuir kinetics dictates that a species can dissociate into two atoms upon adsorption. This understanding of a single gas phase molecule producing two adsorbed species results in a half order dependence for the adsorbed species as derived from Langmuir kinetics. In corroboration with the experimental data for species concentration dependence, this

analysis can be viewed as additional support for the proposed reaction mechanism. The kinetic parameters measured in the following discussion uses half order dependence on steam concentration.

In the current research, experiments were run from 973-1273 K for approximately one hour over a surface area of 50.65 cm^2 at three different flow rates of steam. A new, un-oxidized rod was inserted into the reactor between each experiment. The flow rates were adjusted throughout the hour of oxidation and the experimental results at each temperature for the three different flow rates are presented in Table 2 as volumetric flow rates per reactive area. Each flow rate corresponds to steady-state production over 5 minutes from six separate experiments. Figure 5 is a plot of the volumetric production rates with respect to temperature for each of the different flow rates. In addition, the production rates from the low temperature experiments under a steam flow rate of 12.5 mL/min are also provided in the plot. When combined with the previous data set for temperatures between 670-875 K in the Arrhenius form, kinetic parameters can be realized from the curve in Figure 6. It has previously been stated that hydrogen produced during this process is thermodynamically favorable based on chemical equilibrium up to temperatures around 1200 K. The activation energy calculated from the slope of the line in Figure 6 is 47.3 kJ/mol and is consistent with the previously reported low temperature hydrogen production calculation. However, there is an apparent outlier in the data at 1073 K, which creates a kink in the Arrhenius curve. This observed kink suggests a change in effective activation energy and can be associated to a thermodynamic effect or even the presence of diffusion limitations. From Figure 1, thermodynamic favorability for the oxidation of iron under steam exists below temperatures of 950 K at equilibrium and that beyond this temperature, the reduction of iron oxide by hydrogen becomes favorable. At higher temperatures, the reduction of iron oxide will compete with the oxidation step causing a decrease in hydrogen production rates. From Figure 6, the change in the kinetic data occurs around 950 K which corresponds to the thermodynamic data, but the effect on the kinetic results is not what would be anticipated from thermodynamic limitations. The production rate does not increase from 875-975 K however, it rapidly increases for temperatures of 1075 and 1175 K, which more closely corresponds to a transition between a reaction rate limited regime to a diffusion limited regime. More data points would need to be gathered to have a better understanding in what is actually occurring, however what can be concluded is that the oxidation of iron from steam should not be done at temperatures that greatly exceed 1273 K. This conclusion is made due to the presence of both diffusion limitations along with competing reactions due to thermodynamic constraints. The impact this may have on syngas production is worth noting due to the dependence of iron oxidation from CO_2 to produce CO. Based upon the same thermodynamic analysis presented for chemical equilibrium of Equation 2, CO production is favored at elevated temperatures well beyond 1173 K. The kinetic results provided later in this article along with the expected reduction temperatures around 1573 K suggest that syngas production would occur at temperatures beyond the thermodynamic favorability of hydrogen production. In order to

optimize the oxidation step for both hydrogen and CO production, an understanding in combined process efficiency is imperative.

3.2 CO Production Analysis

Iron was oxidized under the influence of CO₂ under the same criteria as the high temperature hydrogen production experiments. The oxidation process resembles the previously depicted hydrogen production reaction with steady state CO production rates occurring throughout the reaction with a small downward trend during the extent of reaction due to diffusion limitations. CO production rates were quantified using the previously described process and assumptions. Oxidation results from CO₂-splitting are shown below in Table 3 for each of the three flow rates of CO₂ and graphically represented in Figure 7 for temperatures of 973-1373 K with each point corresponding to an average production rate over 5 minutes. The analysis for CO₂ was done based on the model of kinetic-limited reactions presented for hydrogen production. The production rates for CO were quite low and steady over the 1 hour oxidation and correspond to slow oxide growth rates. Even at these elevated temperatures the oxide layer thickness over the one hour experiment should only represent a negligible barrier to diffusion of reactive ions.

Again, kinetic data was calculated based on rate limiting conditions for obtaining activation energies and pre-exponential constants. Figure 8 is an Arrhenius plot that corresponds to CO production from a CO₂ supplied flow rate 12.5 mL/min. The activation energy and pre-exponential factor was estimated from a linear relation that fit well to the lower temperatures of 973-1173 K but at the higher temperatures, the same pattern occurs that was presented in the high temperature hydrogen production where a decrease occurs in the production rate followed by a rapid increase in the production rate. This occurrence is further discussed later in this report. The values for activation energy and pre-exponential factor are tabulated in Table 4 for each of the flow rates. The previous value for activation energy of ~50 kJ/mol for water-splitting was associated to the water disassociation step as the rate limiting step due to the relation of the activation energy to the reported energies for water chemisorption on magnetite. The activation energy reported here of ~35 kJ/mol for the CO₂-splitting process can likewise be identified as the disassociation of CO₂ into CO and O[•]. The following mechanism represents a Cabrera-Mott reaction pathway for the oxidation of iron by CO₂.

Reaction 14 is consistent with the analysis done by de la Pena O'Shea et al, who demonstrated the activation of CO₂ on cobalt surfaces [37]. This study was duplicated by Glezakou and Dang for activation of CO₂ on iron surfaces and the decomposition energy barrier of CO₂ was estimated to be 5.0 kcal/mol [38]. This energy barrier of about ~25 kJ/mol reported by Glezakou and Dang again shows the importance of the species dissociation step as the rate limiting step.

As with the higher temperature water-splitting experiments, a kink in the Arrhenius curve was identified that demonstrated an apparent increase in activation energy. Figure 9 is a plot of two Arrhenius curves from the water splitting data with the solid line being the previously depicted curve and the dashed line corresponding only to the four high temperature data points. Figure 10 shows one Arrhenius curve that corresponds to the four temperatures discussed earlier for CO₂-splitting along with a second dashed line curve for 1273 and 1373 K separately. The change in the kinetic data occurs around 1273 K so two additional points at 1323 and 1423 K were experimentally measured and plotted along with the second dashed line curve. The trend with both species splitting processes is that once a certain temperature is achieved, production rates begin to change much more rapidly as temperature increases resulting in much higher activation energies. This result appears to reflect a transition between a kinetic limited regime and a diffusion limited regime. The activation differed from 50kJ/mol to 88kJ/mol for water-splitting and 35 kJ/mol to 130 kJ/mol for CO₂-splitting. It is desirable to add additional data points in this region with any future work. In an attempt to assign an uncertainty to the 130 kJ/mol activation energy, the curve was refit using various subsets of the four data points. Based on the standard deviation of the resulting slopes, an uncertainty of 41 kJ/mol is representative. These values are consistent with published kinetic constants that were estimated by fitting diffusion models to experimental data. Mehdizadeh et al found that for their iron-silica porous structure used for water splitting hydrogen production, an activation energy of 88 kJ/mol can be estimated when fitting a first order model that is dependent upon a hybrid of diffusion and boundary controlled mechanisms [39]. The transition between the two regimes is also interesting in that an apparent negative slope (i.e. negative activation energy) is present, which could indicate possible surface morphological changes within this temperature range. There could also be some internal chemistry occurring due to trace amounts of species within the bulk material, such as carbon. This occurrence could be further investigated in order to identify more conclusively what is taking place by evaluating data at additional temperatures, or by cycling the temperature for a given experiment.

3.3 CO₂-splitting Chemical Phase Analysis

As explained in the previous study for low temperature hydrogen production, Raman spectroscopy appears to be sensitive to the presence of hematite with the 613 cm⁻¹ peak being an order of magnitude higher than the magnetite peak at 664 cm⁻¹. Because those two peaks show similar intensities when analyzed from the oxidized species, magnetite is concluded as the resultant oxide formed during water splitting. Raman spectrum were taken of two samples after oxidation experiments run at 1173 and 1373 K and are displayed in Figure 11. Represented by

the red arrow, the magnetite peak found at a Raman shift of 664 cm^{-1} shows an increased intensity value when compared to the magnetite standard response in Figure 12. This again demonstrates that magnetite is the abundant oxide that forms during CO_2 -splitting even though hematite peaks are present. Figures 13 and 14 show EDS images for oxidized species from CO_2 -splitting with a corresponding SEM image for temperatures of 1173 and 1273 K respectively. The SEM images show a well-developed oxide layer on the order of ~ 15 microns, which is expected for oxide development at these temperatures for one hour experiments. In EDS image maps presented below, each of the SEM images represent oxygen response in the left image and iron response on the right. Where the oxide appears to be in the SEM image, oxygen shows a strong response detailing the significant oxide layer presence. The right image depicts the bulk iron with a slightly softer response to iron in the oxide layer as expected. The oxide in Figure 14 appears to be of the same thickness even though oxidized at a higher temperature resulting in more production of CO. This re-illustrates the dependence of oxide layer integrity to extent of reaction or oxide growth. The SEM image shows a much more aggressive topography for the oxide layer, resembling spallation occurrence. As with water splitting, it is recommended that oxidation steps for CO_2 -splitting remain short to limit oxide thickness growth and preserve material integrity. The point scan results in Figure 15 shows the EDS O/Fe ratios normalized to the average oxygen to iron ratio at the center of the oxide layer, which reveals a slight gradient as oxygen response decreases toward the bulk iron. This again further corroborates the Cabrera-Mott model as the source reaction mechanism, where the oxygen and iron ions diffuse toward the middle of the oxide layer and react.

3.4 Iron Alloy Oxidation

To date, all oxidation results discussed in this dissertation were the product of interaction with initial pure iron. The reduction step that will ultimately drive the thermal process to temperatures that exceed 1573 K will limit the effectiveness of iron as a useful material. The higher temperatures will prevent oxides from reducing by causing them to melt, while this could also lead to deactivation of the pure iron core for further oxidation steps. Cobalt oxides have been found to be actively reduced thermally at temperatures as low as 1473 K with similar results for nickel at slightly higher temperatures. If these alloys can be combined with iron to strengthen the thermal properties of the material while promoting the thermal reduction tendencies, a major hurdle in utilizing solar driven fuel production would be overcome. Obtaining iron monoliths with a significant loading of cobalt, nickel or a mixture of both and investigating fundamental oxidation kinetics of those ferrites would be of great interests for the advancement of this technology. How the ferrite oxidation characteristics compare to pure iron sources would be a major influence when associated to thermal reduction improvement. While iron would still be the motivating factor in the oxidation process, it cannot be assumed *a priori* that the kinetics would follow that of pure iron; therefore depending on how a material like cobalt interacts with the iron and mediates oxygen transfer; there could be significant effects in production behavior.

Surepure monoliths were obtained that are an alloy of iron (55%), nickel (28%) and cobalt (17%). The monoliths were again 0.64 cm diameter rods and upon receiving the species, EDS was done to ensure the alloy loading. These species were prepared and oxidized in the same manner as the previous iron species for CO₂-splitting for temperatures of 1073-1373 K. The production rates of CO are displayed in Table 5 and illustrated in Figure 16. At the lower temperatures, when the kinetics are much slower, the rate comparison to the pure iron CO₂-splitting results from Table 3 reveal differences that range from 68-86% during the 12.5 mL/min supply flow of CO₂. The higher flow rates have an increased relation up to about 96% of the pure iron flow rate. This is not consistent with the 55% loading of iron for the same available surface area, and suggests the other components of the alloy may also be oxidizing to form nickel and or cobalt oxides. Another consideration for this result may be that due to the slow kinetics at lower temperatures, the smaller loading does not have a strong effect on reaction. At the higher temperature of 1373 K, there is a decrease in CO production for the oxidation of the alloy of 50-60%, which is consistent to the loading of iron in the alloy and signifies the oxidation of iron as the dominate mechanism during reaction. This would favor that at lower temperatures, the production rates would be less dependent upon loading. The high activity of the surface of the iron allows the production rates to be maintained when kinetics are slower while promoting the thermal properties of the material for increased reduction temperatures. Figure 17 shows an SEM image of the oxidized alloy at 1273 K on the left with a clear oxide layer developed on the surface of the bulk alloy. The image on the right is an EDS species signal map where the highlighted points represent oxygen response. As presented, oxygen response occurs strongly within the oxide and shows almost no response within the bulk material, which is consistent with the previously shown EDS data. Figure 18 displays the EDS signal response map for the 3 species of the alloy with iron being the top image, cobalt the bottom left image and nickel the bottom right. What the images show is iron being abundantly present throughout the bulk material and oxide layer in the top image but the other two species components only showing strong signals within the bulk material from their respective images. From EDS on the bulk alloy, the percentage of iron was found to be substantially less than the reported loading before oxidation but within the oxide only iron was found to have a significant signal. This suggests that the cobalt and nickel do *not participate* in the oxide layer development during the oxidation step. Such a finding has potential impact on the use of mixed metal ferrite materials in a solar furnace for species splitting fuel production, which may preferentially produce iron oxides. Furthermore, this finding continues to support the Cabrera-Mott model as the driving mechanism for the oxidation of iron, as iron was found to leave the bulk alloy matrix during oxidation, selectively diffusing and with the resulting iron oxide being formed on the surface of the alloy.

4. Conclusion

The objective of the study into monolith iron species oxidation by the flow of steam and CO₂ was to identify the fundamental kinetic parameters and reaction mechanisms that pertain to the independent species splitting processes. The results presented in the previous sections

detailed activation energies and pre-exponential coefficient constants that can be used to model these reactions in larger scaled reactors with either porous or particle based iron species. An understanding of the possible reaction pathways and kinetic dependencies allows for accurate reactor optimization and system efficiency. The study did find reaction limitations that pertained to extent of reaction and reaction temperature. As reaction rate increases due to temperature and oxide layer growth become more pronounced, production limitations are presented due to a loss in material integrity along with an increase in diffusion limitations. The study into iron oxide morphology showed that at increased thickness of magnetite oxide layers, species separation or spallation is more prevalent, which can result in the loss of active material. Likewise, as diffusion effects become the limiting factor on reaction rate, competing kinetic parameters cause increases in reaction rate along with an increase in activation energy. At temperatures beyond 1173 K for water splitting and 1273 K for CO₂-splitting, the previously presented results show large increases in reaction rates as temperature changes, along with a significant increase in activation energies. The influence this may have on large scale reactor design and system parameters is apparent in that for certain temperatures production rates may vary based on reaction limitations. For a cyclic process where both reduction and oxidation of iron will occur, the temperature of the reduction process is limited based on effective oxygen release rates. The practical low end of reduction temperatures has been previously discussed and identified to be around 1573 K. For practical solar furnace operation between reduction steps and oxidation steps to be maintained, the difference in temperature between each step would need to be minimized. This would more than likely require the oxidation steps for both species splitting processes to be well within the diffusion limited kinetic range even when short oxidation steps are considered for limited oxide layer development. Another factor on temperature is the effect thermodynamics could play on process efficiency. Because CO₂-splitting will occur at elevated temperatures above 1273 K the thermodynamics will be actively favorable for CO generation and the chemical reduction step of CO₂ generation should not play a competing role during the process. However, as temperature rises, water splitting rates will begin to compete with chemical reduction of iron by H₂. It is also possible for thermal reduction to inhibit both oxidation steps at temperatures above 1373 K causing a decrease in peak species production. Based on the analysis presented here it is recommended to maintain reactor temperatures for the oxidation of iron species to below 1373 K.

Acknowledgements

This work was supported in part by the US Department of Energy, National Energy Technology Laboratory (DE-FE0001321) and Advanced Research Projects Agency-Energy (DE-FOA-0000471).

References

- [1] Barber J. Biological solar energy. *Phil Trans R Soc A* 2007;365:1007-23.
- [2] Abanades S, Le Gal A. CO₂ splitting by thermo-chemical looping based on Zr_xCe_{1-x}O₂ oxygen carriers for synthetic fuel generation. *Fuel* 2012;102:180-6.
- [3] Stamatiou A, Loutzenhiser PG, Steinfeld A. Solar syngas production via H₂O/CO₂- splitting thermochemical cycles with Zn/ZnO and FeO/Fe₃O₄ redox reactions. *Chem Mater* 2010;22:851-9.
- [4] Coker E, Rodriguez M, Ambrosini A, Miller J, Stechel E. Using in-situ techniques to probe high-temperature reactions: thermochemical cycles for the production of synthetic fuels from CO₂ and water. *Powder Diffraction* 2012;27(2):117-25.
- [5] Allendorf M, Diver R, Siegel N, Miller J. Two step water splitting using mixed-metal ferrites: Thermodynamic analysis and characterization of synthesized materials. *Energy Fuels* 2008 22:4115-24.
- [6] Steinfeld A, Sanders S, Palumbo R. Design aspects of solar thermochemical engineering-a case study: Two step water splitting cycle using the Fe₃O₄/FeO redox system. *Sol Energy* 1999;65(1):43-53.
- [7] Galvez M, Loutzenhiser P, Hischier L, Steinfeld A. CO₂ splitting via two-step solar thermochemical cycles with Zn/ZnO and FeO/Fe₃O₄ redox reactions: thermodynamic analysis. *Energy Fuels* 2008;22:3544-50.
- [8] Loutzenhiser P, Galvez M, Hischier L, Steinfeld A. CO₂ splitting via two-step solar thermochemical cycles with Zn/ZnO and FeO/Fe₃O₄ redox reactions II: kinetic analysis. *Energy Fuels* 2009;23:2832-9.
- [9] Venstrom L, Petkovich N, Rudisill S, Stein A, Davidson J. The effects of morphology on the oxidation of ceria by water and carbon dioxide. *J Sol Energy Eng.* 2012; 134.
- [10] Steinfeld A. Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. *Int. J Hydrogen Energy* 2002;27:611-9.
- [11] Neises M, Roeb M, Schmücker M, Sattler C, Pitz-Paal R. Kinetic investigations of the hydrogen step of a thermochemical cycle using mixed iron oxides coated on ceramic substrates. *Int J Energy Research* 2010;34:651-61.

- [12] Gokon N, Murayama H, Umeda J, Hatamachi T, Kodama T. Monoclinic zirconia-supported Fe₂O₃ for the two-step water-splitting thermochemical cycle at high thermal reduction temperatures of 1400-1600°C. *Int J Hydrogen Energy* 2009;34:1208-17.
- [13] Smestad G, Steinfeld A. Review: Photochemical and thermochemical production of solar fuels from H₂O and CO₂ using metal oxide catalysts. *Ind Eng Chem Res* 2012;51:11828-40.
- [14] Loutzenhiser P, Meier A, Steinfeld A. Review of the two-step H₂O/CO₂-splitting solar thermochemical cycle based on Zn/ZnO redox reactions. *Materials* 2010;3:4922-38.
- [15] Li H, Zhang J, Young D. Oxidation of Fe-Si, Fe-Al and Fe-Si-Al alloys in CO₂-H₂O gas at 800°C. *Corrosion Sci* 2012;54:127-38.
- [16] Kim J, Johnson T, Miller J, Steechel E, Maravelias T. Fuel production from CO₂ using solar-thermal energy: system level analysis. *Energy Environ Sci* 2012;5:8417-29.
- [17] Loutzenhiser P, Steinfeld A. Solar syngas production from CO₂ and H₂O in a two-step thermochemical cycle via Zn/ZnO redox reactions: thermodynamic cycle analysis. *Int J Hydrogen Energy* 2011;36:12141-7.
- [18] Stamatiou A, Loutzenhiser P, Steinfeld. Solar Syngas production from H₂O and CO₂ via two-step thermochemical cycles based on Zn/ZnO and FeO/Fe₃O₄ redox reactions: kinetic analysis. *Energy Fuels* 2010;24:2716-22.
- [19] Loutzenhiser P, Stamatiou A, Steinfeld A. Concentrated solar energy for thermochemical producing liquid fuels from CO₂ and H₂O. *Energy Conversion* 2011;63(1):32-4.
- [20] Vannice MA. An analysis of the Mars-van Krevelen rate expression. *Catal Today* 2007;123:18-22.
- [21] Routray K, Reddy KRSK, Deo G. Oxidative dehydrogenation of propane on V₂O₅/Al₂O₃ and V₂O₅/TiO₂ catalysts: understanding the effect of support by parameter estimation. *Appl Catal A Gen* 2004;265:103-13.
- [22] Arnold E, Sundaresan S. The role of lattice oxygen in the dynamic behavior of oxide catalysts. *Chem. Eng. Comm.* 1987;58:213-30.
- [23] Routray K, Deo G. Kinetic parameter estimation for a multiresponse nonlinear reaction model. *AIChE J* 2005;51:1733-46.
- [24] Shee D, Rao M, Deo, G. Kinetic parameter estimation for supported vanadium oxide catalysts for propane ODH reaction: Effect of loading and support. *Catal Today* 2006;118:288-97.

- [25] Mars P, van Krevelen DW. Oxidations carried out by means of vanadium oxide catalysts. *Chem Eng Sci* 1954;3(1):41-59.
- [26] Roberts M, Wood P. The mechanism of the oxidation and passivation of iron by water vapour- an electron spectroscopic study. *J Electron Spectrosc Relat Phenom* 1977;11:431-7.
- [27] Roberts MW. Mechanism of the oxidation of iron films at temperatures from -195°C to 120°C. *Trans Faraday Soc* 1961;57:99-109.
- [28] Mott N. The theory of the formation of protective oxide films on metals, II. *Trans Faraday Soc* 1940;39:472-83.
- [29] Mott N. Oxidation of metals and the formation of protective films. *Nature* 1940;145:966-1000.
- [30] Mott N. The theory of the formation of protective oxide films on metals, III. *Ibid* 1947;43:429-34.
- [31] Cabrera N, Mott NF. Theory of the oxidation of metals. *Rep Prog Phys* 1948;12:163-84.
- [32] Roeb M, Gathmann N, Neises M, Sattler C, Pitz-Paal R. Thermodynamic analysis of two-step solar water splitting with mixed iron oxides. *Int J Energy Research* 2009;33:893-902.
- [33] Svoboda K, Slowinski G, Rogut J, Baxter D. Thermodynamic possibilities and constraints for pure hydrogen production by iron based chemical looping process at lower temperatures. *Energy Convers Manag* 2007;48:3063-373.
- [34] Svoboda K, Slowinski G, Rogut J, Baxter D, Pohorely M. Thermodynamic possibilities and constraints for pure hydrogen production by a nickel and cobalt-based chemical looping process at lower temperatures. *Energy Convers Manag* 2008;49:221-31.
- [35] Charvin P, Abanades S, Flamant G, Lemort F. Two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production. *Energy* 2007;32:1124-33.
- [36] Stehle R, Bobek M, Hooper R, Hahn D. Oxidation reaction kinetics for the steam-iron process in support of hydrogen production. *Int J Hydrogen Energy* 2011;36:15125-35.
- [37] De la Pena O'Shea V, Gonzalez S, Illas F, Fierro J. Evidence for spontaneous CO₂ activation on cobalt surfaces. *Chem Phys Lett* 2008;454:262-8.
- [38] Glezakou V, Dang L. Spontaneous activation of CO₂ and possible corrosion pathways on the low-index iron surface Fe(100). *J Phys Chem C* 2009;113:3691-6.

[39] Mehdizadeh A, Klausner J, Barde A, Rahmation N, Mei R. Investigation of hydrogen production reaction kinetics for an iron-silica magnetically stabilized porous structure. *Int J Hydrogen Energy* 2012 ;37:13263-71.

Figure Captions:

Figure 1: Gibbs free energy change with respect to temperature (left) along with moles of produced hydrogen and CO with respect to temperature (right) for Reactions 1 and 2.

Figure 2: High temperature thermal reactor design for oxidation of iron that can be implemented for both hydrogen production and CO production.

Figure 3: Iron monolith supported within high temperature furnace by stainless steel noose.

Figure 4: Hydrogen production rate with respect to water concentration at 800 K (left) and a Log-log plot of hydrogen production rate with respect to water concentration (right).

Figure 5: Hydrogen produced from Iron oxidation under the influence of steam.

Figure 6: Arrhenius curves for the oxidation of iron under the influence of steam.

Figure 7: CO Produced from Iron Oxidation Under the Influence of CO₂.

Figure 8: Arrhenius curve for the oxidation of iron under the influence of CO₂ supplied at 12.5 mL/min.

Figure 9: Comparison of Arrhenius curves for the full temperature range (600-1275 K) and the high temperature range (875-1275 K) for water splitting.

Figure 10: Comparison of Arrhenius curves for the full temperature range (973-1373K) and the high temperature range with two additional points (1273-1423K) for CO₂-splitting.

Figure 11: Resulting Raman spectra for oxidized species after CO₂-splitting.

Figure 12: Raman signal responses for iron oxide reference standards.

Figure 13: SEM image and EDS point scan mapping for a 1173 K oxidized iron rod from CO₂-splitting.

Figure 14: SEM image and EDS point scan mapping for a 1373 K oxidized iron rod from CO₂-splitting.

Figure 15: Normalized oxygen to iron ratios measured from EDS signals along the extent of the oxide layer following CO₂-splitting.

Figure 16: CO Produced from Iron Alloy Oxidation Under the Influence of CO₂.

Figure 17: SEM image and EDS point scan mapping for a 1273 K oxidized iron alloy rod from CO₂-splitting.

Figure 18: EDS mapping of Fe (top), Co (Bt. Right) and Ni (Bt. Left) to illustrate the oxide layer being primarily iron oxide.

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9:

Figure 10:

Figure 11:

Figure 12:

Figure 13:

Figure 14:

Figure 15:

Figure 16:

Figure 17:

Figure 18:

Table Captions:

Table 1: List of set flow rates during oxidation experiments at higher temperatures (1073-1473K).

Table 2: Produced H_2 volumetric flow rates for each of the 3 flow rates of H_2O during a reaction time of 1hr.

Table 3: Produced CO volumetric flow rates for each of the 3 flow rates of CO_2 during a reaction time of 1hr.

Table 4: Kinetic constants calculated from the Arrhenius forms displayed in Figure 4-17.

Table 5: Produced CO volumetric flow rates for each of the 3 flow rates of CO_2 during a reaction time of 1hr.

Table 1:

Species	Helium (4.5 UHP Grade)	Argon (4.8 UHP Grade)	Liquid Water	CO ₂ (4.0 UHP Grade)
	(cc/min)	(cc/min)	(μ l/min)	(cc/min)
	100	200	12.5	12.5
Flow Rate	100	200	25	25
	100	200	50	50

Table 2:

Water Flow Rate	Average Production Rate (mL/min cm ²)* (RSD)		
	12.5 mL/min	25 mL/min	50 mL/min
973 K	0.0139 (23%)	0.0178 (15%)	0.0219 (7%)
1073 K	0.0149 (13%)	0.0226 (19%)	0.0334 (16%)
1173 K	0.0638 (24%)	0.0891 (16%)	0.1435 (9%)
1273 K	0.1336 (27%)	0.1701 (24%)	0.2179 (23%)

*Volumetric flow defined at 298 K and 1 atm.

Table 3:

CO ₂ Flow Rate	Average Production Rate (mL/min cm ²)*		
	(RSD)		
	12.5 mL/min	25mL/min	50 mL/min
973 K	0.0053 (14%)	0.0084 (3%)	0.0112 (14%)
1073 K	0.0077 (22%)	0.0097 (11%)	0.0145 (8%)
1173 K	0.0106 (13%)	0.0138 (12%)	0.0206 (17%)
1273 K	0.0097 (11%)	0.0130 (11%)	0.0202 (14%)
1373 K	0.0209 (3%)	0.0322 (5%)	0.0552 (7%)

* Volumetric flow defined at 298 K and 1 atm.

Table 4:

CO ₂ Flow Rate	Kinetic Constants		
	12.5 mL/min	25 mL/min	50 mL/min
E _{eff} (kJ/mol)	32.8	31.8	37.9
A (mol ^{1/2} / cm ^{1/2} s)	8.8	8.1	8.8

Table 5:

CO ₂ Flow Rate	Average Production Rate (mL/min cm ²)*		
	(percent ratio of alloy production rates to pure iron sample rates)		
	12.5 mL/min	25mL/min	50 mL/min
1073 K	0.0070 (76%)	0.0091 (85%)	0.0147 (95%)
1173 K	0.0079 (68%)	0.0092 (65%)	0.0141 (69%)
1273 K	0.0089 (86%)	0.0109 (92%)	0.0171 (93%)
1373 K	0.0134 (63%)	0.0164 (52%)	0.0253 (47%)

*Volumetric flow defined at 298 K and 1 atm.