Progress in an Oxygen-Carrier Reaction Kinetics Experiment for Rotary-Bed Chemical Looping Combustion

by

Jack Jester-Weinstein

Submitted to the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science at the Massachusetts Institute of Technology June 2013

© 2013 Jack Jester-Weinstein All rights reserved

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part in any medium now known or hereafter created.

Signature of Author.......................................................... Department of Mechanical Engineering May 10, 2013

Certified by.......................................................... Ahmed F. Ghoniem
Ronald C. Crane (1972) Professor of Mechanical Engineering Thesis Supervisor

Accepted by.......................................................... Anette Hosoi
Professor of Mechanical Engineering Undergraduate Officer
Progress in an Oxygen-Carrier Reaction Kinetics Experiment for Rotary-Bed Chemical Looping Combustion

by

Jack Jester-Weinstein

Submitted to the Department of Mechanical Engineering on May 10, 2013 in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science.

ABSTRACT

The design process for an experimental platform measuring reaction kinetics in a chemical looping combustion (CLC) process is documented and justified. To enable an experiment designed to characterize the reaction kinetics of the reduction/oxidation cycle in a rotary channeled oxygen carrier, a platform was designed to deliver controlled conditions of temperature and gas flow around a central disc of oxygen-carrier material and determine the rates of oxidation and reduction using real-time gas analysis (RTGA). In order to deliver precise and accurate results, it was necessary to identify and either minimize or compensate for interfering factors such as gas turbulence, temperature fluctuation, and flow equipment response time delays. This paper serves as a progress report on the experimental reactor; the overall design process is discussed, including equipment selection, reactor design, electronics and control hardware setup, and software interface design, and the current state of the reactor is discussed, including an assessment of the current capabilities and drawbacks of the system, future work, and potential methods for improvement.

Thesis Supervisor:
Ahmed F. Ghoniem
Ronald C. Crane (1972) Professor of Mechanical Engineering

Direct Supervisor:
Claire Chen
Master’s Candidate, Mechanical Engineering
ACKNOWLEDGMENTS

The publication of this thesis marks the end of a challenging and exciting college experience and ushers in the beginning of a career as a professional engineer. I could not have made it to where I am today without a number of amazing people, and I would like to salute just a few of them.

First, I would like to thank Professor Ahmed Ghoniem, thesis supervisor and role model, for giving me the opportunity to work on truly cutting-edge thermal systems research, and for his excellent tutelage in project engineering and thermodynamics.

Thank you Claire Chen for the first-rate experience we had working together. May your data always come out cleanly.

Thank you Thomas Peacock for the example you set and for your caring guidance over the years.

Thank you Brandy Baker for keeping me honest and helping me through the final hurdles of thesis preparation.

And lastly, a thank you to my loving and wonderful parents, to whom I owe everything I am and for whose support I will never cease to feel blessed; to Maja and Robin, with whom I will be overjoyed to share this moment; and to Drew, who I know would have been proud.
# TABLE OF CONTENTS

Abstract .................................................................................................................................................. 3
Acknowledgments .................................................................................................................................. 4
I. Introduction ......................................................................................................................................... 6
II. Background ........................................................................................................................................ 9
   Chemical Looping Combustion ........................................................................................................ 9
      Overview ...................................................................................................................................... 9
      Reactor Design ............................................................................................................................ 10
      Oxygen Carrier Selection .......................................................................................................... 10
   Solid Rotary-Bed CLC Reactor ......................................................................................................... 12
      Results from Rotary-Bed CLC Simulation .................................................................................. 13
   Oxygen Carrier Performance: Experimentation ............................................................................. 14
III. Experimental Reactor Design .......................................................................................................... 16
   OC Sample Preparation .................................................................................................................. 16
   Instrumentation Selection ............................................................................................................. 16
      Direct measurement: Thermogravimetric Analysis (TGA) ....................................................... 17
      Indirect measurement: Real-Time Gas Analysis (RTGA) ......................................................... 18
   Reactor Implementation ................................................................................................................ 20
   Electronics and Control .................................................................................................................. 22
   Software Interface Design ........................................................................................................... 25
IV. Reactor Platform Assessment .......................................................................................................... 28
   Hardware Testing & Performance ................................................................................................... 28
      Timing and Flow Considerations for RTGA Data Collection ................................................ 29
      Synchronizing Data Collection ................................................................................................ 30
   Internal Volume Estimation ......................................................................................................... 31
      Internal Gas Mixing through Diffusion and Eddy Convection ................................................. 32
V. Future Work ...................................................................................................................................... 34
   Next Steps: Software ..................................................................................................................... 34
   Next Steps: Electronics Hardware .................................................................................................. 35
   Calibration and Testing .................................................................................................................. 35
      Determination of internal volume .............................................................................................. 35
      Flow mixing characterization ...................................................................................................... 37
      Oxygen Transfer Capacity Comparison with TGA ................................................................. 37
   Potential Improvements to the Reactor System .......................................................................... 39
      Internal Volume Reductions ....................................................................................................... 39
      High-Temperature Residence Time Reductions ....................................................................... 41
      Data Processing ......................................................................................................................... 41
V. Conclusion ......................................................................................................................................... 42
Nomenclature ........................................................................................................................................ 43
Works Cited .......................................................................................................................................... 44
I. INTRODUCTION

In recent years, an increasing body of evidence has amassed to demonstrate that accumulation of atmospheric carbon dioxide will lead to significant global surface warming and climate change. The urgency of global climate change has led to significant attention in recent decades toward reduction of carbon emissions. Some global political momentum has been gained with efforts such as the Kyoto Protocol, an international agreement through the United Nations which mandated a 5% reduction in carbon emissions versus 1990 levels between 2008-2012 [1]. In order to enable the significant reductions needed to ensure climate stability, however, it will be necessary to develop improved low-carbon technologies that will allow emissions reductions while maintaining the current standard of living.

Carbon capture for fossil fuel generation is one of the To date, attention toward “green” or low-carbon energy sources has largely been focused on renewable-energy sources such as wind, solar, tidal, and biomass power. Despite progress in these technologies, though, fossil fuels remain the most economical source of energy, and the share of global energy provided by fossil fuels is projected to remain above 75% through 2035 [2]. Technology capable of decreasing the carbon dioxide emissions of fossil fuel systems without prohibitive cost increases could thus have a significant impact on carbon emissions. Carbon capture and storage (CCS) offers a means to reduce the environmental impact of fossil fuel power production by diverting CO₂ from power plant exhaust, liquefying it, and placing it into storage. Energy-economic modeling has shown that mature CCS technology could significantly lower the cost of global carbon emissions reductions. However, the cost of CCS is still high relative to that of power production without carbon capture [3]. Multiple technologies are currently under development that could lower the cost of CCS; Figure 1 shows the reductions in cost penalty with a set of increasingly advanced CCS technologies.
Figure 1. Cost of electricity increase for IGCC plants versus power production without CCS, comparing current CC technology (A) and CC technologies currently under development (B-G). Taken from Rubin et al. 2012 [3]

Chemical-looping combustion (CLC) – shown in Figure 1 as column G – is among the most promising technologies for high-efficiency, low-cost CCS currently under development. CLC uses a circulated metal oxide (termed oxygen carrier, or OC) as an oxygen transfer medium to integrate oxygen separation into the combustion reactor, allowing oxyfuel combustion without the efficiency penalties of cryogenic separation. CLC is currently in the prototype stage, with numerous units built on the order of 0.5-10 kW [4]. However, significant challenges remain in the implementation and scaling of CLC.

In order to overcome difficulties in scaling, controlling and optimizing reactors imposed by the fluidized-bed designs currently dominating CLC research, the MIT Reacting-Gas Dynamics Laboratory is currently investigating a novel CLC reactor using a rotating metal oxide-coated monolith in place of a fluidized bed of metal oxide particles. A recent paper published by Zhenlong Zhao of the novel rotary-bed reactor [4] simulated the reactor performance and demonstrated high efficiency and output capacity.

As part of this research effort, the RGD Laboratory is building an experimental reactor which will be used to validate the simulation by examining the reaction kinetics of planar oxygen carriers subjected to gas flow. The rate at which OCs can uptake and release oxygen is key to determining the power density and thus the size and cost of a rotary-bed reactor; thus this experiment will verify one of the key assumptions in the simulation and inform the development of larger rotary-bed prototypes.
This thesis addresses the engineering challenge of designing and building the oxygen-carrier characterization reactor. As the reactor is still under construction, this paper will act as a progress report, detailing the engineering process involved in designing and building the reactor, what has been done to date, and what remains to be done for implementation. Finally, an assessment will be made of the capabilities of the experimental platform as it is currently implemented and ways in which it could potentially be improved or adapted to expand functionality.
II. BACKGROUND

Chemical Looping Combustion

Overview

The chemical looping process integrates the oxygen separation process into the combustion reaction, avoiding the costly efficiency penalties imposed by cryogenic oxygen production. To accomplish this integration, a metal oxide is utilized to transfer oxygen between separate channels of fuel and air. The metal oxide, termed an oxygen carrier in this process, reacts with gaseous fuel at high temperatures and is reduced to a pure metal or reduced oxide, yielding a pure stream of carbon dioxide and water for CO₂ capture. The oxygen carrier is then regenerated to its original metal oxide by reaction with air. The enthalpy for the net reaction is the same as that from conventional combustion. Depending on the specific oxygen carrier, the reduction with fuel can be either endothermic or slightly exothermic, while the oxidation in air is highly exothermic.

\[
\begin{align*}
N_2, O_2 & \quad \text{Oxidation reaction} \\
\text{Air} & \quad \text{Me}_xO_y \\
\text{Reduction reaction} & \quad \text{CO}_2, \text{H}_2\text{O} \\
\text{Me}_xO_{y-1} & \quad \text{Fuel}
\end{align*}
\]

Figure 2. General process for CLC. Taken from Adanez et al. [5]

Reactor Design

The majority of existing CLC reactors utilize an interconnected fluidized-bed design, in which particulate oxygen carrier material is exchanged between separate fluidized-bed reactors, with an air-reactor for oxidation and a fuel-reactor for combustion. The majority of designs feature a high-velocity riser for air and a low-velocity bubbling bed for fuel, motivated by the need for higher residence times for oxidation. However, a variety of designs have been proposed utilizing different configurations of fluidized beds. Alternating packed-bed designs would reduce the necessary volume and allow operation at higher pressure, but lead to significant complexity in gas switching and heat transfer [5]. Finally, Dahl et al. proposed a rotary packed-bed design in which a single cylindrical bed rotates oxygen-carrier material through flows of air and fuel.
Oxygen Carrier Selection

The material used as an oxygen carrier (OC) is key to the design and performance of CLC reactors. In order to achieve material stability, OCs are typically composed of a fine particulate metal oxide held together into larger particles by a binder material. Nickel (NiO/Ni), copper (CuO/Cu, Cu₂O/Cu), manganese (Mn₃O₄/MnO, Mn₃O₄/MnO), cobalt (Co₃O₄/Co, CoO/Co), and calcium sulfide (CaSO₄/CaS) are among the most promising materials currently under consideration [4].

Characteristics of OCs that affect the performance and competitiveness of CLC include the following:
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Explanation</th>
<th>Determining equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>The rate at which an OC uptakes oxygen from air and release to fuel</td>
<td></td>
</tr>
<tr>
<td>Oxygen transport</td>
<td>The mass proportion of oxygen carried by an OC material</td>
<td>$R_{OC} = x_{OC} \left(\frac{m_o - m_r}{m_o}\right)$</td>
</tr>
<tr>
<td>capacity</td>
<td></td>
<td>$m_o = \text{mass when fully oxidized}$</td>
</tr>
<tr>
<td>Stability</td>
<td>The ability of an OC to last through a number of cycles without losing oxygen transport capacity</td>
<td>Assuming exponential decay, $\lambda = -\frac{1}{x_{OC}} \frac{dx_{OC}}{dt}$</td>
</tr>
<tr>
<td>Selectivity</td>
<td>The tendency of an OC to form different combustion products (CO₂, H₂O, CO, &amp; H₂) in reaction</td>
<td>$K_{eq,1}(T) = C_{H_2O}/C_{H_2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_{eq,2}(T) = C_{CO_2}/C_{CO}$</td>
</tr>
</tbody>
</table>

Other practical concerns in OC selection include the cost of preparation; the environmental impact of OC production and used OC disposal; the deposition of carbon onto the material’s surface; and, for fluidized-bed designs, the fluidizability of the particulate OC, along with the tendency of the OC to agglomerate at high temperature and its tendency to undergo attrition/fragmentation.
**Solid Rotary-Bed CLC Reactor**

A new design for CLC, developed by the MIT Reacting Gas-Dynamics Laboratory, utilizes a channeled monolith similar to those used by rotary desiccant wheel dehumidifiers.

![Diagram of a rotary desiccant wheel. From Ge et al. [6]](image)

In the proposed rotary-bed design, the bed of fluidized OC is replaced by a cylindrical monolith, a disk passed through with numerous parallel thin channels. The walls of each channel consist of a bulk layer of rigid ceramic coated with an OC material consisting of porous binder and metal oxide. The bulk layer provides rigidity and allows heat transfer between channels, while the porous layer allows for oxygen transfer between successive pulses of fuel and air. With sufficiently thin channels (the proposed opening width is 2 mm) the monolith can have a specific surface area competitive with those found in fluidized bed designs. Since the same channels pass air and fuel streams intermittently, the entire rotary bed also acts as a rotary heat exchanger between the two streams, maintaining a relatively flat temperature profile and reducing exergy losses in the combustion reaction.

![Diagram of (a) individual channel structure, including bulk and porous layers and gas flow path and (b) cross-section showing oxygen carrier coating on the surface of the support layer. Taken from Zhao 2012 [4]](image)
The reactor's vertical channels ensure that gas flow will be unidirectional through the reactor bed. However, in order to avoid direct contact between air and fuel inside the channel, it is necessary to pass a neutral purge gas through the channels between each pulse of air and fuel. This prevents direct combustion from creating points of high temperature which might damage the OC material and lead to exergy losses. For this reason the reactor is designed with two purging sectors which pass steam, likely regenerated from the exhaust stream, as a buffer between air and fuel. This layout is shown in Figure 6.

Figure 6. Diagram of a rotary CLC system design with (a) bottom view showing channels for each gas flowing through the reactor and (b) an isometric projection of the reactor bed showing rotary seals between sectors. From Zhao 2012 [4]

This design has the potential to avoid the disadvantages of fluidized-bed reactors — including fluidized-bed solids transport concerns, reactor corrosion from repeated particulate impact, oxygen-carrier agglomeration, and runaway reactor size with scaling — as well as the gas dilution and mixing problems inherent in a rotary packed-bed design.

Results from Rotary-Bed CLC Simulation

As a first pass at predicting the behavior of the rotary-bed reactor, Zhao modeled the chemical processes in a single channel of the monolith [4]. Zhao selected CuO/Cu as an oxygen carrier with a boron nitride (BN) support as OC material after literature review, and characterized the size, structure, and operating conditions of a concept reactor. The operating characteristics of Zhao's simulated reactor are shown in Table 2.
Table 2. Operating conditions of a simulated rotary-bed CLC reactor.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal operating temperature</td>
<td>1000 °C</td>
<td>Channel length</td>
<td>1.3 m</td>
</tr>
<tr>
<td>Pressure</td>
<td>10 atm</td>
<td>Channel width</td>
<td>2.0 mm</td>
</tr>
<tr>
<td>Thermal capacity</td>
<td>1.02 MW</td>
<td>Reactor diameter</td>
<td>1.6 m</td>
</tr>
<tr>
<td>Gas inlet temperature</td>
<td>823 K</td>
<td>Oxygen carrier</td>
<td>CuO</td>
</tr>
<tr>
<td>Gas inlet velocities</td>
<td>0.3-1.0 m/s</td>
<td>Support material</td>
<td>BN</td>
</tr>
<tr>
<td>Porous OC layer thickness</td>
<td>50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total cycle time</td>
<td>48.0 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration of fuel addition</td>
<td>33.0 s</td>
<td>Avg. fuel residence time</td>
<td>6.21 s</td>
</tr>
<tr>
<td>Duration of fuel purge</td>
<td>5.0 s</td>
<td>Avg. steam residence time, fuel purge</td>
<td>3.25 s</td>
</tr>
<tr>
<td>Duration of air addition</td>
<td>8.0 s</td>
<td>Avg. air residence time</td>
<td>1.03 s</td>
</tr>
<tr>
<td>Duration of air purge</td>
<td>2.0 s</td>
<td>Avg. steam residence time, air purge</td>
<td>0.99 s</td>
</tr>
</tbody>
</table>

Having defined the flow rates and timing of gas pulses through a single channel, the gas flow and chemical processes in the channel were modeled quantitatively as functions of time and length along the channel. Adapting a particulate shrinking-core model to a planar case, his model solved the ODEs describing reaction kinetics and heat transfer over successive gas flow cycles until the channel reached a steady state in which the temperature time series was consistent over each cycle. Zhao’s analysis showed that the reactor was able to reach 100% CO₂ separation and 97.6% combustion efficiency, with an exergy efficiency of 81.2%.

**Oxygen Carrier Performance: Experimentation**

As with all forms of CLC reactor design, the performance of the rotary-bed reactor is highly dependent on the behavior of the OC material. To date, efforts to analyze different OC and support materials have examined particulate OCs, and have not assessed OC behavior for planar OC materials or in conditions of channel flow. Zhao was able to adapt existing models for fluidized CLC to predict the likely behavior of an OC washcoat inside the channels of the rotary-bed reactor; however, to verify the single-channel model, and to select the optimal OC material for larger-scale prototypes, it is necessary to experimentally characterize the behavior of promising OCs under channel flow conditions.
The experimental reactor discussed by this paper was developed not only to validate Zhao’s model, but to explore multiple characteristics of each metal oxide/support material pair under consideration. Specifically, the reactor will allow assessment of the following variables:

1. **Rates of oxygen uptake/release**

The instantaneous rates of oxygen uptake and oxygen release from the OC material indicate the reaction rates of oxidation and reduction, allowing calculation of reaction kinetics to determine the material’s reactivity and comparison with the shrinking-core numerical model. Additionally, time integration of the oxygen uptake/release rates will show each OC’s oxygen transport capacity. Finally, the change in reaction rates over multiple cycles can be assessed to determine the stability of each candidate material.

2. **Concentration of exhaust gases**

Additionally, the concentration of CO and CO₂ will need to be determined in order to determine the material selectivity through combustion equilibrium constants.
III. EXPERIMENTAL REACTOR DESIGN

The basic design for this experiment mirrors other high-temperature experiments currently under way in the Reacting Gas-Dynamics Laboratory: A sample of OC material is contained in a temperature-controlled furnace and subjected to gas flow. To simulate channel flow in the simplest case possible, it was decided to use a flat disk of OC, including both base layer and porous layer. In this case, the OC sample disk will be exposed to alternating pulses of air, a neutral gas, and methane, and the exhaust gases will be fed through a real-time gas analysis (RTGA) module to determine the reactions caused by the oxygen carrier.

OC Sample Preparation

The first sample disks created were made using alumina as both bulk and porous layer and treated with copper oxide through wet impregnation; once these have been used to demonstrate the process, further sample disks can be fabricated using BN support material, other metal oxides, and potentially other fabrication techniques as well.

Bilayer (bulk/porous) alumina disks were ordered from Refractron Technologies Corp. The process to be used was adapted from de Diego et al 2005 [7] following a literature review of particulate OC preparation, and works as follows.

1. The alumina disk is immersed in an aqueous solution of 1-2 M Cu-(NO$_3$)$_2$·3H$_2$O for 12 hours at ambient temperature
2. The disk is dried at 60 °C for 24 hours in a muffle oven
3. The disk is calcined in air for 30 minutes at at 550 °C to decompose the impregnated copper nitrate into copper oxide
4. If necessary, the above steps are repeated to increase the ratio of CuO to Al$_2$O$_3$
5. The sample is calcined again for one hour at 950 °C.

The resulting concentration of CuO in the oxygen carrier is to be measured using SEM/EDX.

Instrumentation Selection

One of the first major decisions in the reactor design process was the choice of instrumentation. In determining how to instrument the reaction, we chose between two common instruments, thermogravimetric analysis (TGA) and real-time gas analysis (RTGA). TGA allows direct analysis of the OC oxygen uptake/release by measuring mass with a microbalance, but does not allow for controlled flow over the sample disk; thus RTGA was chosen to instrument the reaction. The RTGA device will provide indirect measurements of oxygen uptake/release by analyzing the reaction products at the reactor's outlet;
this leads to more complicated analysis but allows the system to more closely approximate the rotating-bed design.

**Direct measurement: Thermogravimetric Analysis (TGA)**

TGA is a commonly used technique for measuring processes involving weight change during temperature fluctuations, using highly precise digital balances to track weight change over time and thermocouples to track temperature and correlate to mass change. For the purposes of this experiment, a TGA instrument could be used to determine the change of mass in a small sample of OC material as it is subjected to pulses of air and fuel gas, causing it to gain and lose oxygen. There are multiple precedents in the literature for TGA assessment of OC reaction kinetics; a characteristic mass/time curve for CLC generated by TGA OC-characterization experiments is shown in Figure 7. Using the time series of mass generated by a TGA instrument, the instantaneous reaction rate could be directly and easily calculated from data:

\[
\dot{n}_{O_2} \text{ reacted} = \begin{cases} 
\frac{\dot{m}_{\text{sample}}}{M_{O_2}}, & \text{oxidation} \\
-\frac{\dot{m}_{\text{sample}}}{M_{O_2}}, & \text{reduction}
\end{cases}
\]

Figure 7 shows a diagram of how TGA might be used in this experiment, with a microbalance holding a small sample of OC material in a gas chamber flushed with air or fuel and contained within a furnace to maintain constant temperature.
TGA has several characteristics that make it advantageous for this experiment. It is highly precise, allows for simple analysis, has precedent in the literature, and can be purchased as part of an integrated unit, essentially eliminating the engineering challenge behind the design of the reactor platform. However, TGA is limited in ways that make it less relevant to the rotary-bed CLC case. The maximum mass of the sample is limited; of the units considered for this experiment (TA Instruments TGA-HP50, TGA-HP150, and TGA-HPs), the maximum sample mass was 25 g. Most critically, however, TGA units act as closed systems and do not allow for controlled gas flow through the sample chamber. Instead, TGA units fill the sample chamber with static gas and measure changes as the sample disk reacts with its environment. Without the ability to mirror the planar flow experienced in the rotary disk reactor, this would constitute a significant departure from the phenomenon being modeled.

**Indirect measurement: Real-Time Gas Analysis (RTGA)**

RTGA devices allow chemical analysis of dynamic processes, usually combining a fast-sampling mass spectrometer with intermittent gas chromatography. In this experiment, RTGA could be applied to the combustion products to determine the proportion of each combustion product, providing insight into the combustion equilibrium constants as well as oxygen transfer into and out of the sample. The measurement is indirect, in that the oxygen content of the sample disk cannot be measured directly but only determined by integrating gas flow. This leads to potentially lower accuracy in measurements of the instantaneous rate, as—for example—exhaust products may mix in the tubing between the OC sample and the RTGA.
equipment, distorting the time series. However it allows for analysis of more massive samples than most TGA instruments can handle – since the mass of the sample isn’t limited by the capacity of the TGA microbalance – and allows for experimentation at high pressure and under varying conditions of gas flow.

![Diagram of OC analysis setup with RTGA](image)

**Figure 8.** (a) diagram of a typical OC analysis setup with RTGA; (b) characteristic data produced by RTGA.

After consideration of commercial TGA and RTGA units, it was decided that the advantages of TGA (high precision direct measurement of oxygen uptake) were outweighed by the downsides (inability to test under conditions of hydrodynamic flow and high cost). Additionally, in order to measure both selectivity of the OC sample, it was necessary to include an RTGA unit regardless of whether TGA was used to determine reactivity. Thus, RTGA was selected as the sole instrument for reaction analysis.

The Shimadzu GCMS-QP2010 Ultra, a combined GC/MS unit, was selected for the experiment. The QP2010 Ultra offers a maximum acquisition rate of 100 Hz, fast enough to detect transient changes in combustion products in the transition regimes between oxidation, purge, and reduction phases. The QP2010 also has a high sensitivity (500:1 signal/noise) and a high scan speed (20,000 amu).

Since GC/MS units cannot differentiate between gas molecules with equal mass-to-charge ratio (m/z), the neutral purge gas was selected to have a molecular mass that would result in minimal interference with the combustion products to be analyzed, specifically $O_2$ (m/z = 32 Da), CO (m/z = 28 Da), and CO$_2$ (m/z = 44 Da), and methane (m/z = 16 Da). To reduce the system complexity, it was decided to use dry air, avoiding the need to measure exhaust concentrations of H$_2$O and H$_2$. This made helium gas (He, m/z = 4 Da) an ideal purge gas, as the MS could be set to scan for m/z above 4 and thus avoid registering intensity peaks for He altogether. The interference between methane and CO (for which m/z is the same) is seen as
unavoidable; however, to ensure that these would be visible without interference from N₂ in the air – and to ensure that no foreign compounds or additional species of gas were introduced to the reactor – a synthetic air will be used, with a formulation of 20% O₂ and 80% He.

**Reactor Implementation**

![Diagram of reactor implementation](image)

Figure 9. System schematic showing gas flow paths and information flow from instrumentation to lab computers.

Figure 9 shows the overall system layout for the experimental reactor. Compressed gas cylinders containing each gas to be used in the reaction are connected through tubing to Brooks GF40 mass flow controllers (MFCs), which allow precise control over the gas flow rates and report flow rates from internal flowmeters – allowing acquisition of precise volumetric flow rate data. The outlet tubes from the MFCs are then joined by tees and passed into the furnace, where they flow over the surface of the OC sample disk. The inlet and outlet gases are arranged in counterflow to encourage heat transfer between incoming and outgoing gas streams, and to ensure that flow across the sample disk is largely along the plane of the material surface. The gas leaving the furnace is then transferred to the Shimadzu GC/MS unit.
Stainless steel tubing was used to transport gases in order to resist corrosion from methane and potential temperature variations. Swagelok compression fittings provide a tight seal to ensure that gases are not lost in the process. As a safety precaution, manual ball valves were placed between each gas tank and corresponding MFC, as well as between the tees joining outflow from the MFCs and the inlet to the quartz piping in the furnace, to ensure that gases are not accidentally introduced into the furnace. These safety valves are shown on the system schematic in Figure 9.

Figure 10. (a) Diagram showing counterflow gas flow path; (b) assembled counterflow piping in the furnace

The furnace is intended to be fired to 1000 °C during trials, so quartz tubing was selected as an inert, temperature-resistant material to contain gases within the reactor chamber. The sample sits in the end of a closed 1” O.D. quartz pipe, sized to allow the sample to fit neatly in the bottom, which acts as the outlet. A ¼” O.D. quartz pipe serves as the inlet to the sample. To achieve counterflow, the 1” quartz pipe is connected through a Swagelok screw-tight fitting to stainless steel tubing which is then bushed to a ½” tube and compression-fit cross; the ¼” inlet pipe is passed down through the cross and into the 1” outlet pipe, while the outlet flow is passed out a horizontal arm of the cross. This design and the gas flow through the cross is illustrated in Figure 10.
Note that the fourth arm of the cross is used for a thermocouple feedthrough, which allows a thermocouple to be passed down into the quartz outlet pipe to measure the temperature of gases leaving the reaction. Similarly, the ¼” quartz inlet pipe is teed at the top to a thermocouple feedthrough; that thermocouple is fed down the length of the pipe to measure the temperature of the inlet gases and ensure that they are sufficiently heated before contacting the sample disk.

Exhaust gases from the furnace are then passed through a brass tee ball valve, which allows the researcher to select whether to vent them to the laboratory exhaust line or to pass them to the GC/MS unit. The GC/MS line tees to a pressure gauge to ensure that the pressure remains nominal throughout the reactor. The tee valve is visible in Figure 10b.

**Electronics and Control**

As shown in Figure 9, the instrumentation installed on this experiment to date consists of the GC/MS, which uses Shimadzu software to interface directly with a computer; two thermocouples, one each for incoming and outgoing gas flow from the sample disk inside the furnace; and the four Brooks MFC units, which report flow rates as an analog DC voltage signal. Data acquisition from the thermocouples and MFC units is performed by two National Instruments data acquisition devices (DAQs). An NI USB-6120 multipurpose DAQ is used for analog input, while output to the MFCs is done through a NI-9123 voltage output module in a cDAQ-9171 single-slot chassis. The flow of information between DAQs and instruments is shown schematically in Figure 11.

![Diagram](image)

**Figure 11. Information flow diagram showing signal transmission between DAQ devices and analog instruments.**

The Brooks MFCs allow linear control and data conversion; that is, the set point signal which determines flow rate and the reported flow rate reading from each MFC is scaled linearly so that the 0-5V signal
range corresponds to a flow rate value between 0 sccm and the maximum flow rate of each MFC. The thermocouples are connected to the USB-6120 through Omega Super-MCJ thermocouple-analog converters, which similarly scale the temperature reading from 0-10,000 °C to a linearly corresponding voltage between 0-10V.

Electrical power is provided to the analog instruments and signals are transmitted between the DAQ and instruments by a control box. The control box provides a manual interface for turning on and off power to the MFC units, protects the MFCs from power surges, and breaks out the RS-485 cables which the MFCs use for analog communication into BNC connectors. This allows for flexible, clean, and easily understood connections to the DAQs. Figure 12 shows the schematic of the control box, including a 24V power supply which delivers DC power to the MFCs; 750 mA fuses for surge protection; and terminal blocks breaking out the MFC RS-485 cables to BNC panel-mount jacks.

![Figure 12. Schematic of the electronics control box, which transfers power and signal to the analog instruments.](image-url)
Figure 13 shows the complete electronics setup, including the electronics enclosure. In the absence of a lasercutter or CNC mill, panel cutouts were hand-marked on the enclosure and cut out using a drill press and a Dremel tool. The system and MFC power switches are visible on the front panel; the BNC jacks on the side; and the fuses are contained in fuse holders mounted at the back of the control box under the cable passes for the MFC cables.

Figure 13. DAQs, control box, and thermocouple-analog converters. The red/black cable pairs transfer signal between analog instruments and DAQs. Power switches for each MFC are visible on the front face of the control box.
Software Interface Design

A MATLAB graphical user interface (GUI) was adapted from another RGD Laboratory project to incorporate MFC set point control, MFC/thermocouple readings, and data logging into a single interface. The interface is shown in Figure 14.

![MATLAB graphical user interface](image)

Figure 14. MATLAB graphical user interface for experiment control.

The GUI as it currently stands is designed for a first iteration of the experiment. It gives manual rather than automatic control over gas flow, allowing the researcher to select whether and when to initiate oxidation, reduction, and purging by clicking the appropriately labeled button on the left upper side of the interface. In later versions of the GUI a phase timing feature will be added to allow automatic switching between phases.

The panels along the upper left side of the allow control over the set points for gas flow in each phase. The GUI was hard-coded to know which MFCs should be activated during which phase to ensure that user error cannot cause oxygen and fuel to be fed simultaneously into the reactor. Thus, the researcher may specify the flow rates for air during oxidation, helium during purge, CH₄ during reduction, and helium during reduction at the same time, and the GUI will select which set points to output. The target values sent to each MFC are displayed at the lower left along with the flow rate values received from each MFC.
The panels in the center show real-time graphs of temperature and flow rate data, allowing the user to select which MFC and which thermocouple to track.

The panels to the right display temperature readings and track the total elapsed time of the experiment and the time elapsed in the current phase. The lower right panel allows control over the DAQ sampling rate and notes the destination of the log file. The GUI is designed to log data whenever the experiment is operational, launching a Save As prompt whenever the researcher initializes the experiment by pressing one of the Oxidize/Purge/Reduce buttons for the first time. Data is logged in CSV format using the built-in MATLAB I/O functions fwrite() and dlmwrite().

To ensure consistent DAQ communication at high sampling rates the GUI was migrated from an earlier DAQ interface which used low-level calls to the National Instruments DAQmx library to the MATLAB Data Acquisition Toolbox, a MATLAB-native wrapper for DAQmx that allows easy interface using the NI session interface mode and a listener structure which pushes data from the DAQ Toolbox to the GUI. Figure 15 shows a diagram of the listener structure as used in the GUI software. Upon experiment initialization, a sampling rate and notification rate are written to the DAQ; the DAQ internal clock controls sampling rate and triggers a listener object in software whenever a pre-determined number of samples have been logged. The listener object then calls a listener function which logs data to CSV and refreshes the GUI. This ensures consistent operation with regard to the DAQ and avoids errors from computer/DAQ clock mismatch, which can lead to requests for data that are too frequent, which can deplete the DAQ sample buffer over time, or too infrequent, which can lead to buffer overflow.

As shown in Figure 15, a global data structure stores data for plotting, handles to DAQ toolbox objects and plots, and state variables, allowing access to state variables and GUI-dependent information from inside listener and peripheral functions without object-oriented-style argument passing. Future versions of the code would be more readable if the global data structure were replaced with object-oriented argument passing, although this was not done in this code given the time constraints.
Figure 15. Schematic of GUI software design, showing listener update structure and data flow.
IV. REACTOR PLATFORM ASSESSMENT

This section will discuss the process of validating the reactor’s performance and assessing its capabilities. To date we have confirmed that the DAQs, electronics control box, and GUI each function appropriately on their own, and checked the MFC calibration to ensure that they deliver linear flow rates as well as determine their switching speed. The next step will be to use the GC/MS to assess the properties of gas flow through the reactor, testing for residence time and convective/diffusive gas mixing inside the reactor chamber. These tests are delayed until the GC/MS is reconfigured to rapid sampling, and will likely happen early in Spring 2013.

Finally, this section will look forward and give a preliminary assessment of the capabilities and limitations of the reactor system, addressing concerns with residence time and flow mixing and potential difficulties with rapid automatic cycling.

Hardware Testing & Performance

Before using the MFCs for flow control, we tested their performance to ensure that they were both well-calibrated to deliver flow rates as a linear function of the set point voltage and that they demonstrated fast switching time. Testing of the MFCs shows a strong agreement between voltage set point and resulting flow rate, as expected. However, the MFCs demonstrate a settling time longer than nominal, taking around 2 seconds to reach 90% of the set point flow rate value, as shown in Figure 16. At this point it is unclear whether this delay is internal to the MFC or a problem with the earlier version of GUI code using low-level library calls. The settling time is consistent and roughly independent of the magnitude of set point change, demonstrated in Figure 17.

![Figure 16](image-url)

Figure 16. (a) Correlation of delivered flow rates from MFC to set point. (b) MFC delivered flow rate over time immediately after set point change.
Figure 17. Flow rate from an MFC following a series of step function set point changes.

It is worth noting, however, that at the time of both of these tests the GUI software being used was significantly limited in sampling rate, able to take data only around 1 Hz – too low to resolve the settling curve needed to determine the settling time accurately. These tests will need to be redone using new code with a higher sampling rate.

Timing and Flow Considerations for RTGA Data Collection

The use of RTGA for analysis introduces significant complexity into data acquisition, since the oxidation/reduction state of the sample cannot be directly measured at any time, but only inferred from the exhaust gases leaving the reactor. This introduces a few potential sources of error for which it is critical that we compensate in order to produce meaningful and accurate results:

- Delays introduced by gas residence time inside the reactor may interfere with interpretation of results from the GC/MS.
- Gas mixing inside the reactor may interfere with interpretation of results from the GC/MS.
- Exhaust gases may continue to react after leaving the surface of the sample disk, skewing the reported concentration of reaction products such as CO/CO₂.

To date, the GC/MS unit has not yet been configured for rapid sampling; it was erroneously set up by Shimadzu to use intermittent sampling at a maximum rate of 0.67 samples/mL, corresponding to a maximum sampling rate of 0.2 Hz at a flow rate of 20 mL/min – well below the target sampling rate. The GC/MS is currently being rebuilt, and isn’t yet usable for gas analysis. This has prevented us from running important calibration tests to characterize gas flow through the system. However, it is still possible to make predictions for which tests will be important to run, and what results we might expect to find.
Synchronizing Data Collection

As the reactor is currently set up, the independent variables (the flow rates for each gas introduced into the system and the system temperature) and the dependent variables (concentrations of gas species at the outlet of the reactor) are logged by separate computers – one connected to the DAQs/electronics and another dedicated to control and logging for the Shimadzu GC/MS. The data sources are also subject to a significant time delay due to the residence time of gas in the reactor system. In order to ensure correct correlation between the independent and dependent data logs, we will need to anticipate a time delay between the two data logs for each time point, and another delay between the release of gases from the MFCs – timestamped in the first data log – and the point at which the gases actually reach the sample disk and react. Moreover, both of these factors will vary over time depending on flow rates.

The key variable in determining the input-output delay will be the total volume of the reactor's internal flow path. For a constant flow, the inlet-sample and sample-outlet delays can be calculated solely based on fluid residence time:

\[
\Delta t_{\text{inlet-sample}} = \frac{V_{\text{reactor,inlet to sample}}}{\dot{V}_{\text{fluid}}}
\]

\[
\Delta t_{\text{sample-outlet}} = \frac{V_{\text{reactor,sample to outlet}}}{\dot{V}_{\text{fluid}}}
\]

For initial testing – before the experiment is converted to rapid automatic cycling – the approximation of constant flow may be accurate enough to provide meaningful results. The MFCs are able to provide an accurate constant flow, so the only significant deviation from the assumption of constant flow would occur when the input gas was being switched, which as discussed above takes approximately two seconds. If the duration of each cycle is far greater than the switching time, the time fluctuations imposed by the MFCs during gas switching may be insignificant.

However, once the experiment is converted to rapid cycling, the time of each phase will be on the same order as the switching time, causing flow variations from switching to become significant. At this point, it will be necessary to calculate time delay as a function of time; that is, for each sample taken by the GC/MS, we can identify how long ago the gases being sampled were released by the MFCs by solving the following implicit definition for \(\Delta t\):

\[
\int_{t_{\text{GC/MS sample}} - \Delta t_{\text{inlet-sample}}}^{t_{\text{GC/MS sample}}} \dot{V}_{\text{fluid}}(t) dt = V_{\text{reactor,inlet to sample}}
\]

1 For this section we will neglect any gas mixing through diffusion or convection and work from an assumption of plug flow. Later sections will discuss the effects of gas mixing on data acquisition near gas slug boundaries.
This could easily be solved iteratively for each time point using MATLAB's built-in numerical integration methods.

To date, however, only the constant-flow assumption has been implemented in MATLAB. As shown in Figure 14, the GUI includes a panel which takes in the flow path volumes of the reactor between MFC inlet and sample disk and between sample disk and GC/MS outlet, and calculates the expected inlet-sample and sample-outlet delays. This is not currently saved to disk, as it can be easily calculated again from the flow rate data saved to the log file; however, once automatic cycling is implemented, the integration solver will need to be written and its results added to the log file.

**Internal Volume Estimation**

Once the GC/MS is operational, we will be able to determine the total volume of the system by flowing a gas such as argon across the reactor, compare the timestamps of the MFC turning on and the gas appearing in the GC/MS detector, and calculate the volume from the total time and flow rate using the integral equations developed above. This method will be developed further in Section IV.

Although the GC/MS cannot yet be used, we can still estimate the total volume of the system using measurements of pipe length and the nominal inner diameters of the piping. These calculations are shown in Table 3 and Table 4. It is worth observing that the main contributor to volume in the system is the 1" outer quartz counterflow pipe (shown in Figure 10), which holds 104 mL of gas when the inner quartz counterflow pipe is neglected. This means that gas will have a minimum residence time of 5 minutes inside the furnace after it has made contact with the sample disk.

**Table 3. Volume estimation for inlet flow path (from tee at MFC outlets to sample disk)**

<table>
<thead>
<tr>
<th>Component</th>
<th>I.D. (in)</th>
<th>Length (in)</th>
<th>Volume (in^3)</th>
<th>Volume (cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4&quot; S.S. pipe</td>
<td>0.18</td>
<td>7.25</td>
<td>0.18</td>
<td>3.0</td>
</tr>
<tr>
<td>Plastic tube</td>
<td>0.165</td>
<td>10.75</td>
<td>0.23</td>
<td>3.8</td>
</tr>
<tr>
<td>Inner quartz pipe</td>
<td>0.155</td>
<td>28</td>
<td>0.53</td>
<td>8.6</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>15.4</strong></td>
</tr>
</tbody>
</table>
Table 4. Volume estimation for outlet flow path (from sample disk to reactor system outlet). (Neglects the tubing that will connect the reactor to the GC/MS, which is expected to be small-diameter and thus add negligible volume.)

<table>
<thead>
<tr>
<th>Component</th>
<th>I.D. (in)</th>
<th>Length (in)</th>
<th>Volume (in^3)</th>
<th>Volume (cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer quartz pipe</td>
<td>0.859</td>
<td>12</td>
<td>6.95</td>
<td>114</td>
</tr>
<tr>
<td>1&quot; S.S. pipe</td>
<td>0.875</td>
<td>2.375</td>
<td>1.43</td>
<td>23.4</td>
</tr>
<tr>
<td>1/2&quot; S.S. pipe</td>
<td>0.425</td>
<td>6.875</td>
<td>0.975</td>
<td>16.0</td>
</tr>
<tr>
<td>1/4&quot; S.S. pipe</td>
<td>0.18</td>
<td>11.75</td>
<td>0.299</td>
<td>4.90</td>
</tr>
<tr>
<td>Inner quartz pipe</td>
<td>0.25 (O.D.)</td>
<td>18.5</td>
<td>-0.908</td>
<td>-14.9</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td><strong>153</strong></td>
<td></td>
</tr>
</tbody>
</table>

Note that with an overall volume of 168 mL, the hydraulic residence time of fluid should be roughly 8½ minutes at the maximum flow rate of 20 sccm.

**Internal Gas Mixing through Diffusion and Eddy Convection**

These residence time calculations assume the presence of plug flow – namely, that slugs of gas proceed through the reactor tubing without mixing. The Reynolds number should be on the order of 10^6, as shown in Table 5, meaning that flow should be very laminar, approaching Stokes flow. This means that convective mixing – spatial distortion of the boundary between adjacent gases in the pipes – will not be present inside the pipes of the reactor.

Table 5. Calculation of Reynolds numbers for multiple cases in the reactor.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pipe</th>
<th>Temp (°C)</th>
<th>Kinematic Viscosity (m²/s)</th>
<th>I.D. (m)</th>
<th>Flow Rate (cm³/min)</th>
<th>Flow Rate (m³/s)</th>
<th>Reynolds Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>S.S. 1/4&quot;</td>
<td>20</td>
<td>0.000015111</td>
<td>0.002286</td>
<td>20</td>
<td>3.33333E-07</td>
<td>12.28</td>
</tr>
<tr>
<td>Helium</td>
<td>S.S. 1/4&quot;</td>
<td>20</td>
<td>0.00011731</td>
<td>0.002286</td>
<td>20</td>
<td>3.33333E-07</td>
<td>1.583</td>
</tr>
<tr>
<td>Argon</td>
<td>S.S. 1/4&quot;</td>
<td>20</td>
<td>0.000013416</td>
<td>0.002286</td>
<td>20</td>
<td>3.33333E-07</td>
<td>13.84</td>
</tr>
<tr>
<td>Air</td>
<td>S.S. 1/4&quot;</td>
<td>1000</td>
<td>0.0001851</td>
<td>0.002286</td>
<td>20</td>
<td>3.33333E-07</td>
<td>1.003</td>
</tr>
</tbody>
</table>

However, the gases will still pass over sharp corners inside bushings and around the lip of the inner quartz tube. Each of these has the potential to introduce eddies into the laminar flow, causing convective mixing between adjacent gases.
Additionally, diffusion between adjacent slugs will inevitably cause mixing over the course of the fluid’s progress through the reactor, although the extent to which gases will diffuse into one another in the reactor has not yet been calculated.

Since this experiment measures dynamic behavior, gas mixing in the reactor – depending on the extent of mixing – could lead to significant introduction of error into the results obtained by impairing our ability to determine which gas particles passed by the OC sample disk and were reacted at any given moment. While convective mixing behavior could be predicted through numerical simulation, it will be easier to simply measure the effect of on the residence time distribution of gases passing through the reactor. Section IV will discuss means for measuring the extent of gas mixing, and propose a signal processing technique for reducing the noise introduced by gas mixing if necessary.
V. FUTURE WORK

This section will detail the work remaining to complete the experimental system -- that is, the future work to be done specifically on the reactor hardware and software addressed in this paper. Additionally, it will give a set of recommendations for improvements that might be made on the reactor system.

Next Steps: Software

The software is currently fully functional for use in experiments with researcher-controlled gas switching. However, for later experiments it will be necessary to change the GUI to add automatic cycle control functionality. A mockup of a GUI with automatic cycle control is shown in Figure 18.

![Mockup of GUI with automatic cycle control](image)

Figure 18. Mockup of GUI with automatic cycle control, seen in the central “Cycle Timing” panel.

This automatic cycle control will be able to take advantage of the same framework behind the user-controlled cycle control, and the GUI elements shown in Figure 18 have already been created in MATLAB GUIDE. Thus, the only changes necessary will be to shift the output DAQ from single-shot output mode to continuous output mode within the NI session interface and to add timer functionality that will populate the output voltage time series delivered to the output DAQ.

Additionally, the MATLAB software may benefit from the integration of data processing that will make the results easier for researchers to analyze. Using the assumption of constant time delay, it is possible to
quickly calculate time delay from flow rates or directly from log files using Microsoft Excel. However, especially in the case of rapid automatic cycling—in which the cycle time scale approaches that of the settling time of the MFCs—it may be useful to researchers to build in integral time delay calculations to the MATLAB code to be able to add a projected time delay element to experiment log files.

**Next Steps: Electronics Hardware**

For improved time coordination between computers, we plan to link the MFC control computer to the inlet valve for the GC/MS; this will require adding RS-485 functionality to the MATLAB GUI in order to communicate with the GC/MS valve control. Once this is accomplished, it will allow us to synchronize the sampling performed by both computers by controlling the timing of sampling in the GC/MS directly from MATLAB. Additionally, we may add a three-way solenoid to the exhaust of the reactor to allow for software-controlled switching between exhaust and piping to the GC/MS; this would require altering the controls box to add an additional switch and BNC jacks to interface the DAQs to a solid-state relay. However, neither of these alterations are necessary for full experiment functionality.

**Calibration and Testing**

As discussed in Section III, once the GC/MS has been configured for rapid sampling it will be necessary to test the gas flow behavior through the reactor. This section proposes methodologies for two of these tests, one to determine the internal volume of the reactor and another to determine the extent of gas mixing inside the reactor.

**Determination of internal volume**

It will be critical to know the exact internal volume of the reactor in order to synchronize MFC flow rate data with GC/MS concentration data, as discussed in Section III. This test will allow us to refine the estimate of internal volume by determining the amount of time it takes for a switch in inlet gases to be reflected by the GC/MS. Figure 19 shows a representation of the internal volume calculation on resulting flow rate time series.
Figure 19. Graphical representation of internal volume calculation using flow rates from MFCs and GC/MS.

The procedure will be roughly as follows, and can take place with the furnace completely off such that no reaction occurs:

1. Begin gas flow with high sampling rate on MFCs.
2. Turn GC/MS on to high sampling rate.
3. Ensure timestamps are consistent between computers.
4. Switch between gases once to create a pulse, and wait for it to register on the GC/MS before turning off data acquisition.
5. Determine the appropriate points on the MFC and GC/MS flow rate time series at which the switch occurs (for example, this could be the point at which the measured flow rate of gas is 50% of nominal – further discussion will be needed to choose the exact calculation).
6. Calculate the internal volume according to

\[ V_{\text{reactor}} = \Delta t_{\text{inlet-sample}} \times \dot{V}_{\text{fluid}} \]

7. To differentiate between the volumes of the reactor between inlet and sample and between sample and outlet, it will be necessary to do an additional volume measurement. A few options present themselves:

   a. Since the inlet-sample line is almost exclusively piping, it should be possible to estimate its volume closely by repeating measurements of tube lengths on the inlet line and calculating inlet-sample volume using lengths and inner diameter measurements.
   b. Reconfigure the reactor to use a single MFC connected through a single known length of tubing through to the sample disk, redo the total volume calculation, and subtract the volume of the known length of tubing.
Flow mixing characterization

A similar test will allow us to determine the extent of convective and diffusive mixing in the reactor, to ensure that the boundaries between gases are not convecting or diffusing significantly while passing through the reactor. This will be accomplished by comparing the time series of gas flow in the transition regime between two gas flows and comparing the settling time between that produced by the MFC and that recorded by the GC/MS. Figure 20 compares the ideal results from this test, in which the concentration time series shown by the GC/MS is exactly the same as that reported by the MFC (solid blue curve), with a set of scenarios showing increased degrees of gas mixing (dashed blue curves).

![Figure 20. Hypothetical scenarios depicting increasing degrees of gas mixing within the reactor.](image)

This can be done using the same methodology as the internal volume calculation. If this test demonstrates that gas mixing is significantly impacting the outlet concentration data, it will be necessary to investigate data processing methods to compensate for internal mixing.

Oxygen Transfer Capacity Comparison with TGA

Once the reactor is complete and performing high-temperature reaction trials, we will be able to confirm the validity of our measured reaction rates not only by comparing with the modeled predictions from Zhao, but also by calculating the oxygen transfer capacity (OTC) of the sample disk and comparing with a direct measurement of OTC using TGA. In the ideal case we would be able to use TGA on our own sample disks using a high-mass, high-temperature TGA unit; however this should also be possible using results from the literature.
Although TGA does not allow for kinetics experimentation under hydrodynamic flow, as discussed in Section II, it does allow for direct and accurate measurement of OTC, measured as a mass difference between fully reduced and fully oxidized states:

\[ R_O = \frac{m_o - m_r}{m_o} \]

The equivalent measurement using RTGA is more indirect and thus more vulnerable to error:

\[ R_O = \frac{1}{m_o} \int_0^\infty \left[ \frac{2M_O}{M_{CO_2}} \dot{m}_{CO_2}(t) + \frac{M_O}{M_{H_2O}} \dot{m}_{H_2O}(t) \right] dt \quad \text{(single reduction phase)} \]

These two calculations are shown graphically in Figure 21.

![Figure 21. Calculation of OTC through (a) TGA and (b) RTGA. Image (a) adapted from Adanez 2004 [8]](image)

In order to ensure that our measurement of reaction rates is accurate, we can confirm the OTC as follows:

1. Create a sample disk as outlined in Section II.
2. Use SEM and mass measurements to determine the mass of metal oxide impregnated in the sample disk.
3. Determine the expected OTC of the sample disk either directly using TGA or using a best estimate from a characterization of our OC material in the literature.
4. Perform a single reduction cycle, allowing the reaction to go to completion (until no CO\textsubscript{2} or H\textsubscript{2}O register in the GC/MS readings).
5. Integrate the flow rates of CO\textsubscript{2} and H\textsubscript{2}O over the time of the reaction to determine the measured OTC.
6. Calculate the error in the measured OTC versus the expected OTC.

If we find low error in this calculation, it will demonstrate clearly that the system produces accurate instantaneous reaction rates. Otherwise, it will indicate some error either in our measurements or our data processing, and will thus serve as a validation for our experimental results.

**Potential Improvements to the Reactor System**

It may be possible to improve the reactor's accuracy and the speed at which it can cycle through gases by making some modifications to the platform hardware and software. These largely fall into three categories: hardware changes which would reduce the internal volume of the reactor; hardware changes which would specifically reduce residence times at high temperature; and software changes which would improve data processing.

**Internal Volume Reductions**

Reducing the internal volume of the reactor could have multiple benefits to the reactor. First, longer residence times will allow for increased gas mixing, both through diffusion and eddy convection. Second, long residence times lead to long delays between release of gases from the MFCs and detection by the GC/MS, hampering the researcher's ability to respond to and analyze transient behaviors in the reactor. Thirdly, longer residence times inside the furnace allow combustion products to continue reacting. As the reactor is currently built, gases will spend 4-5 minutes inside the furnace at 1000 °C. These high residence times are incidental to the reactor construction, and could be reduced significantly without needing to alter the reactor's function.

As seen previously in Table 4, by far the largest contributor to the internal volume of the reactor is the outer quartz pipe inside the furnace, constituting roughly 60% of the total volume, followed by the components used to bush the outer quartz pipe back down to 1/8” tubing (that is, the stainless steel components shown in Figure 10). Thus, the most significant internal volume reductions are also those which would reduce the residence time of gases in the furnace. Other volume reductions, such as replacing the 1/8” piping with 1/16” or 1/32”, would require significantly more effort for lower yield.

Reducing the internal volume in the furnace could take the form of either modifying or replacing the quartz counterflow pipe setup. Modifying the counterflow pipes has the advantage of being easier and more easily reversible than replacing them entirely, so we shall consider them first. One option for reducing internal volume without changing the setup would be to thread a thin steel tube (~1/32”) into the quartz pipes and extract a small portion of the combustion products immediately after contacting the disk to feed directly into the GC/MS. However, this would require additional flow control to make sure that
the flow rate down this line was known and constant and would also require a demonstration that the combustion products are consistent radially and axially across the surface of the sample disk. An easier approach would to fill a significant portion of the volume of the quartz pipe with a smooth nonreactive material such as alumina. A \( \frac{3}{4}'' \) O.D. filler material flush against the inner quartz pipe would reduce the internal volume of the outer pipe to 27 mL, eliminating 45% of the total estimated internal volume of the reactor, and reducing the residence time of gas in the furnace by 74%.

![Diagram of the counterflow pipes with a filler material for internal volume reductions.](image)

Figure 22. Diagram of the counterflow pipes with a filler material for internal volume reductions.

The volume of the stainless steel components could also be significantly reduced by replacing components. The counterflow setup requires the inner quartz tube to be passed through SS tubing with at least 3/8” O.D., leaving room to reduce volume by eliminating the 1” section of steel piping. By ordering a custom reducing compression fitting to attach the outer quartz tubing directly to a \( \frac{1}{2}'' \) tube, the total volume could be reduced by 23 mL, or 13%. Similarly, replacing the cross compression fitting with a reducing cross that allows reduction directly to 1/8” (which might need to be custom ordered) could reduce the volume by 8 mL, or 5%.

Alternatively, the counterflow setup could be replaced completely by a tube-shaped OC sample. This has already been considered for the project, and is a potential next step for experimentation. A tubular OC sample could be press-fit to steel tubes without need to increase the inner diameter at any point; a 3/16” I.D. OC sample could lead to furnace internal volumes of approximately 10 mL, roughly 1/3 of the
volume of the modified counterflow setup, and roughly half the total internal volume. Using a tubular OC sample gives the additional benefit that the gases would be exposed to a greater surface area of OC material and over a much greater fraction of their residence time in the reactor, reducing the proportion of time in which gases are left to react on their own and introduce noise into the combustion-product selectivity measurements.

The OC sample tubes could still be prepared through the same wet-impregnation technique; however, integrating them would require more effort to implement. In order to keep the OC sample at constant temperature, it would need to be kept short and fully contained within the furnace; thus we wouldn’t be able to use compression fittings, and would need to press fit the sample tube between two sections of steel, quartz, or alumina pipe. This would require modification of the table on which the furnace is mounted to allow the press fit.

**High-Temperature Residence Time Reductions**

In addition to these modifications to reduce the internal volume, other means might be used to reduce the residence time of gases at high temperature. Increasing gas flow rates would reduce the residence time in the furnace but also reduce contact time with the sample and potentially increase convective mixing.

The most obvious option for increasing gas flow rates would be to exchange the MFCs currently in use for units with higher maximum flow rate and increase each flow of gas proportionally. However, this could lead to a higher noise-to-signal ratio, as the rate at which gas reacts with the OC would not change significantly, leading to a small proportion of gas conversion at higher flow rates. Another option would be to dilute each gas stream with a constant flow of helium, which would not change the proportion of gas consumption among the gases detectible by the GC/MS. Either of these options, however, would reduce the gas contact time with the sample proportionally to the furnace residence time, potentially slowing down the OC reaction; they would also increase the Reynolds number of flow, which would lead to increased presence of eddies in the reactor and thus increased convective mixing.

Unrelated to residence time inside the furnace, we might consider quenching the gases exiting the furnace. An expander such as a nozzle would cool the gases immediately after leaving the furnace, but might introduce turbulent mixing that would increase noise in the GC/MS results. Instead, the gases could be passed through thin metal tubing in an ice bath.

**Data Processing**

Despite reductions in internal volume, some degree of diffusive and convective eddy mixing will be unavoidable in the reactor. These could be compensated for using signal processing techniques in
software. We can conceive of the delay and mixing behavior of the reactor as a system function acting on the input flow rate time series delivered by the MFCs in order to generate an output flow rate time series, that measured by the GC/MS. Using the data from an unreacting trial such as those described above for internal volume calculation, a technique such as Wiener deconvolution could be used to determine the system function from the MFC and GC/MS flow rate data. GC/MS data from all further experiments could then be convolved with the inverse of the derived system function to reduce the losses of accuracy from mixing and delay. This would require implementation in MATLAB as a separate post-processing script, and should only be undertaken if deemed necessary.

VI. CONCLUSION

In conclusion, this paper has presented an overview of the current state of an experimental reactor for planar CLC oxygen-carrier characterization. The reactor consists of an OC sample contained in a temperature-controlled furnace, with gas flow controlled by mass-flow controllers and reaction analysis performed using real-time gas analysis from an integrated GC/MS unit. The reactor hardware and software are close to complete, with a few steps remaining to implement software-controlled automatic gas cycling. Critically, the GC/MS has not yet been configured for rapid sampling, delaying gas flow characterization tests which will be crucial in validating the reactor design. The high residence time of gases inside the furnace and the potential for error introduction through internal gas mixing were addressed, and recommendations made for how to assess the significance of each error source and potential means to compensate. An overall assessment of the accuracy of the experiment cannot be made until the reactor has been tested with the GC/MS; however it promises to shed light on an important aspect of the MIT RGD's novel rotary-bed CLC reactor, and provide a critical stepping stone from simulations to larger-scale prototypes.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{OC} )</td>
<td>Oxygen transport capacity of oxygen carrier sample, including both inert support compounds (i.e. alumina) and active metal/metal oxide material.</td>
<td>[kg/kg]</td>
</tr>
<tr>
<td>( R_O )</td>
<td>Oxygen transport capacity of the metal/metal oxide in isolation.</td>
<td>[kg/kg]</td>
</tr>
<tr>
<td>( x_{oc} )</td>
<td>Percentage of oxygen carrier that consists of active metal/metal oxide.</td>
<td>[kg/kg]</td>
</tr>
<tr>
<td>( m_o )</td>
<td>Mass of oxygen carrier sample when fully oxidized</td>
<td>[kg]</td>
</tr>
<tr>
<td>( m_r )</td>
<td>Mass of oxygen carrier sample when fully reduced</td>
<td>[kg]</td>
</tr>
<tr>
<td>( M_X )</td>
<td>Molecular weight of molecule X (i.e., ( \text{O}_2 ))</td>
<td>[kg/mol]</td>
</tr>
<tr>
<td>( \dot{n}_{O_2 \text{ reacted}} )</td>
<td>Molar reaction rate of ( \text{O}_2 ) between oxygen carrier and fuel stream</td>
<td>[mol/s]</td>
</tr>
<tr>
<td>( \dot{V}_{\text{fluid}} )</td>
<td>Mass flow rate of gas through the system</td>
<td>([\text{m}^3/\text{s}])</td>
</tr>
<tr>
<td>( t_{\text{GC/MS sample}} )</td>
<td>When considering the effects of flow on timing, the time at which a data point containing an arbitrary molecule of gas passes through the GC/MS ionization chamber and is analyzed.</td>
<td>[s]</td>
</tr>
<tr>
<td>( \Delta t_{\text{inlet-sample}} )</td>
<td>The duration of time elapsed between when an arbitrary molecule of gas enters the inlet of the reactor system and when it encounters the sample disc.</td>
<td>[s]</td>
</tr>
<tr>
<td>( \Delta t_{\text{sample-outlet}} )</td>
<td>As above, the duration of time between contacting the sample disc and entering the outlet of the reactor system</td>
<td>[s]</td>
</tr>
</tbody>
</table>
WORKS CITED


