The images on the front cover showcase the wide variety of interdisciplinary research being conducted in the Swanson School of Engineering at the University of Pittsburgh.

PICTURED CLOCKWISE:

Scanning electron microscopy image of nickel-based alloy 625; page 44 by Eamonn Hughes, Department of Mechanical Engineering and Materials Science

Proposed pathway for heterolytic dissociation of hydrogen and its binding to a Lewis pair; page 102 by Benjamin Yeh, Department of Chemical and Petroleum Engineering

Axial compression test of p. Pubescens (Moso) culms-a bamboo specimen; page 17 by James R. Bumstead, Department of Civil and Environmental Engineering

Pre-operative CT scan image of a patients’ thoracic aorta; page 62 by Thomas G. Kappil, Department of Bioengineering

Graphical representation of spike trains observed in neurons of a macaque monkey; page 79 by Stephen C. Snow, Department of Electrical and Computer Engineering

BACKDROP IMAGE:

Scanning electron microscopy image of black silicon; page 67 by Mohamed A. Kashkoush, Department of Industrial Engineering
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A Message from the Associate Dean for Research

*Ingenium* is Latin for “natural capacity” or “invention.” Some argue that the word “engineer” was derived from the word “engine.” As civil engineer John Wier once wrote, “the roots of [both] ‘Ingenium’ and ‘Engineer’ mean ‘to do, to act, or to make’. While the aim of the scientist is ‘to know’; the aim of the engineer is ‘to do’. What we do, as “doers”, is apply science to our work.” The University of Pittsburgh Swanson School of Engineering proudly presents the second edition of *Ingenium: Undergraduate Research at the Swanson School of Engineering* to celebrate the “ingenium” inherent in the practice of engineering.

*Ingenium* is a compilation of reports representing the achievements of selected Swanson School undergraduate students who demonstrated excellence in our summer research program during the summer of 2015. The students studied mostly under the tutelage of a faculty mentor in the Swanson School of Engineering. In a few cases, the work was performed in Pitt’s School of Medicine or even at other institutions, both in the United States and abroad. At the conclusion of the program, students were asked to submit abstracts summarizing the results of their research, which were then reviewed by the *Ingenium* Editorial Board made up of Swanson School graduate student volunteers. The authors of the highest ranking abstracts were invited to submit full manuscripts for consideration in *Ingenium*, and those that were submitted were peer reviewed by the Editorial Board.

*Ingenium*, therefore, is more than a record of our undergraduate students’ excellence in research; it also serves as a practical experience for our undergraduate students in scientific writing and the author’s perspective of the peer review process and provides practical experience for our graduate students in editorial review and the reviewer’s perspective of the peer review process.

I would like to acknowledge the hard work of the co-editors-in-chief of this edition of *Ingenium*, Sudhanshu Shekhar and Amir Mostafaei, and the production assistance of Melissa Penkrot and Marygrace Reder. Also, this edition would not have been possible without the hard work of the graduate student volunteers who constitute the *Ingenium* Editorial Board (individually listed on page 6). It also is appropriate to thank the faculty mentors and other co-authors of each of the reports included in this edition.

On behalf of U.S. Steel Dean of Engineering Gerald Holder and the entire Swanson School of Engineering community, I hope that you enjoy reading this second edition of *Ingenium* and that the many talents of our students inspire the engineers of the future!

![David A. Vorp, PhD](image)

David A. Vorp, PhD
Associate Dean for Research
University of Pittsburgh Swanson School of Engineering
A Message from the Co-Editors-in-Chief

Greetings and a warm welcome to the second edition of Ingenium: Undergraduate Research at the Swanson School of Engineering. After countless hours of revision and preparation, we are proud to present the second edition on behalf of the entire Ingenium team. As the only peer-reviewed undergraduate research journal at the University of Pittsburgh, Ingenium serves to fill the gap between the high prospects of student research and the available opportunity for publication. This goal could not have been fulfilled without the expertise, dedication, and support of our editorial board and faculty advisors as well as the perseverance and patience of our contributing student authors. We thank all of them for their valuable insights and efforts and applaud them for their achievements and for helping Ingenium showcase the great potential that exists within undergraduate research here at Pitt’s Swanson School of Engineering.

Ingenium was started as an initiative to showcase the wide variety of interdisciplinary research conducted by our diverse and vibrant undergraduate researchers. We are honored to share the work of so many committed and thoughtful people. In this edition, you will find a collection of articles from each department within the Swanson School covering a huge variety of topics spanning both the experimental and the theoretical and ranging from the nano to the industrial scale. As a reader, we hope that you will not only appreciate the multidisciplinary nature of this publication but also gain a glimpse into the many research opportunities that the Swanson School has to offer.

Each paper presented in this edition underwent the common two-step peer review process involving evaluation of extended abstracts and full manuscripts. We are thankful for the tireless efforts of the editorial board, which is composed of outstanding graduate students at the Swanson School. These reviewers contributed their time and expertise to this project on a volunteer basis.

Additionally, we are grateful to Associate Dean for Research David A. Vorp, PhD, for his thoughtful and effective guidance; to Melissa Penkrot for her invaluable help and advice; to Marygrace Reder and the Department of Communications Services for their production assistance; to our brilliant contributors; and, of course, to you, the reader, from whom the entire process and presentation of research derives its significance. Finally, we wish to encourage more contributions from the authors and reviewers to ensure a continued success of future editions of Ingenium.

Amir Mostafaei
Co-Editor-in-Chief

Sudhanshu Shekhar
Co-Editor-in-Chief
Editorial Board Members

Ingenium: Undergraduate Research at the Swanson School of Engineering

Co-Editors-in-Chief:

Amir Mostafaei (Mechanical Engineering and Materials Science) and Sudhanshu Shekhar (Bioengineering)

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Optimization of Processing Parameters of Additively Manufactured Inconel 625 and Inconel 718

Glen Ayes*, Zhenyu Liu, Brian Gleeson, and Guofeng Wang*
Department of Mechanical Engineering and Materials Science, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, PA, USA

Abstract
The Laser Engineered Net Shaping (LENS®) method of additive manufacturing with Inconel 625 (IN625) and Inconel 718 (IN718) powders deposited onto low-carbon steel substrates was investigated. Utilizing the Taguchi method, nine experiments for each powder were conducted based on an L9 orthogonal array with the processing parameters laser power (W), laser speed (mm/s), and powder feed rate (g/s) studied, each at three levels. Unevenness, wall height, and middle height of the samples were measured and implementing grey relational grade analysis and analysis of variance (ANOVA) allowed for the identification of optimum parameters and the contribution of each parameter on deposit geometry. Energy area density (EAD (J/mm²)) and energy mass density (EMD (J/g)) were calculated and EAD vs. EMD was graphed in order to predict whether an incomplete or relatively even sample will occur for combinations of parameters not directly studied. Results revealed the optimum parameters for IN625 as 300 W, 14.8 mm/s, and 0.225 g/s. For IN718, the optimum parameters were found to be 330 W, 14.8 mm/s, and 0.18 g/s. Powder feed rate was shown to have the greatest effect on deposit geometry for IN625, and similarly, laser speed had the greatest effect on deposit geometry for IN718, with contributions of 49.6% and 44.0%, respectively.

Keywords: Inconel; Taguchi method; Deposit geometry; Grey relational grade analysis; Energy area density; Energy mass density.

Introduction
Additive manufacturing (AM) has been around since the 1980s, but there has been a rapid expansion of applications in the past few years [1]. Additive manufacturing is an evolving process with applications ranging from engineering and construction to military and human tissue replacement. The Laser Engineered Net Shaping (LENS®) method of additive manufacturing utilizes powder feeding nozzles that feed powder into the path of a laser to create a deposit on a substrate; rather than, for example, using a powder bed in Selective Laser Melting. LENS® is typically used with metallic powders with grain structure able to be controlled, but since many variables can affect grain structure, further research into this method is required. Inconel 625 (IN625) and Inconel 718 (IN718) are both nickel-chromium based superalloys known for their high strength and corrosion resistance, and their ability to retain their high strength at elevated temperatures [2, 3]. For these reasons, they prove especially useful in aerospace applications, such as in turbine blades [1]. Processing parameters, which include laser power, laser speed, and powder feed rate, influence several aspects of a sample. For instance, inapt settings may lead to adverse conditions, such as initiation of the “balling effect” [4-9] or insufficient energy input [10], consequently leading to increases in porosity and deviation from desired deposit geometry [7-10]. This study aims to optimize the three processing parameters: laser power, laser speed, and powder feed rate, to yield optimal deposit geometry of IN625 and IN718 samples through the application of the Taguchi method, grey relational grade analysis, and analysis of variance (ANOVA) [11-14].

Methods and Materials
In this study, an Optomec LENS® 450 was used to deposit cubic IN625 and IN718 samples. Utilizing a 400 W Fiber Laser, along with four powder feeding nozzles, argon atomized IN625 and IN718 samples were deposited onto 1/8x3x3 in. low carbon steel substrates. Argon gas filled the work chamber to minimize oxidation during the deposition process. Laser power, laser speed, and powder feed rate, each at three levels, were studied via the Taguchi method to obtain optimum parameters. Nine experiments (out of the possible 27, based on the three levels studied for three processing parameters) of each powder were deposited based on the L9 orthogonal array shown in Table 1. It is worth noting that powder feed rate in
Table 1. Combinations of processing parameters employed based on L9 Orthogonal Array

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Power (W)</th>
<th>Speed (mm/s)</th>
<th>Feed Rate (g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>270</td>
<td>14.8</td>
<td>0.135</td>
</tr>
<tr>
<td>2</td>
<td>270</td>
<td>16.9</td>
<td>0.180</td>
</tr>
<tr>
<td>3</td>
<td>270</td>
<td>19.1</td>
<td>0.225</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>14.8</td>
<td>0.135</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>16.9</td>
<td>0.225</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
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</tr>
<tr>
<td>8</td>
<td>330</td>
<td>16.9</td>
<td>0.135</td>
</tr>
<tr>
<td>9</td>
<td>330</td>
<td>19.1</td>
<td>0.180</td>
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</tbody>
</table>

g/s was converted from rpm (rotations per minute) of 9 (0.135 g/s), 12 (0.180 g/s), and 15 (0.225 g/s) by collecting powder at varying rpm over five-minute periods and weighing the powder in order to establish powder feed rate, as shown in Table 1. This conversion to g/s was necessary for calculation of EMD.

Laser scan direction rotated 45° between each layer in order to alleviate anisotropy [5], and layer thickness was set to 0.381 mm for all samples with a total intended height of 10.7 mm. Each sample was cut along the vertical cross section, polished, and etched with 15 mL hydrochloric acid, 10 mL nitric acid, and 10 mL acetic acid. The cross sections were measured for unevenness along the layers within the bottom, middle, and top sections, represented by the red arrows in Figures 1 and 2, and the average value of these three readings was presented as the unevenness value of a sample. The wall height and middle height of the samples were measured with a Neiko digital caliper prior to cutting to obtain deviation from intended sample height (10.7 mm) and to help distinguish levels of failure between partially deposited samples. Energy area density (EAD (J/mm²)) and energy mass density (EMD (J/g)) were both calculated and graphed against each other (relating the three parameters) in order to identify a viable processing range [11]. Equations for EAD and EMD are EAD = \(P/(V*D)\) and EMD = \(P/M\) where \(P\): laser power (W), \(M\): powder feed rate (g/s), \(V\): laser speed (mm/s), and \(D\): laser beam diameter (0.583 mm).

Data Processing

The raw data for unevenness, wall height, and middle height (presented in Table 2) were initially normalized based on targets of either smaller-the-better:

\[ Y = (L - X) / (L - S) \]  

or nominal-the-better:

\[ Y = 1 - |X - N| / \max[L - N; N - S] \]

Where \(Y\): normalized value, \(L\): largest valued raw data, \(X\): raw data being normalized, \(S\): smallest valued raw data, and \(N\): nominal target value. Max[] means that the larger of the 2 calculated values in the brackets was the one used in the equation. Equation (1) was

![Figure 1. Vertical cross section of IN625 experiment 4. Unevenness was measured at red arrows](image1)

![Figure 2. Vertical cross section of IN718 experiment 4. Unevenness was measured at red arrows](image2)
used for normalizing unevenness data since the target value for unevenness was 0 mm. For both wall height and middle height, equation (2) was used with the nominal target value of 10.7 mm. Next, grey relational coefficients conveying the relationship between the target normalized value of 1 and the actual normalized value were calculated.

\[ C = \frac{\Delta \min + \zeta \cdot \Delta \max}{\Delta X + \zeta \cdot \Delta \max} \]  

(3)

Where \( C \): grey relational coefficient, \( \Delta \min \): minimum deviation sequence \((1 - \max(Y))\), \( \Delta \max \): maximum deviation sequence \((1 - \min(Y))\), \( \Delta X \): deviation sequence of \( X \) valued data \((1 - X)\), \( \zeta \): distinguishing coefficient with \( 0 \leq \zeta \leq 1 \). The distinguishing coefficient is used to give weight to different parameters; generally each parameter is given a weight of \( \zeta = 0.5 \). In this study, different weights were used and the reasoning for this will be clarified in the discussion. Following normalization and calculation of grey relational coefficients with equation (3), a grey relational grade for each parameter at each level was computed by averaging the grey relational coefficients for unevenness, wall height, and middle height at the specified level of each parameter [11-12, 14]. Finally, ANOVA was performed on the grey relational grades and determined the contribution of factors into the deposit geometry.

### Results

The largest grey relational grades for levels of laser power, laser speed, and powder feed rate revealed the optimum parameters for IN625 to be 300 W, 14.8 mm/s, 0.225 g/s, respectively. Similarly for IN718, 330 W, 14.8 mm/s, and 0.18 g/s were found to be optimum parameters. Table 3 reports the results of ANOVA performed on the grey relational grades of both IN625 and IN718 samples. For IN625, powder feed rate was found to have the largest contribution to deposit geometry with a 49.6% contribution, followed by 25.3% from laser power, and 24.8% from laser speed. For IN718, laser speed had the greatest contribution of 44.0%, powder feed rate had a 40.9% contribution, and laser power had a 3.52% contribution. Unfortunately, five of the IN625 samples and one of the IN718 samples were incomplete deposits.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inconel 625</th>
<th>Inconel 718</th>
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<tr>
<td>Power</td>
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<td>SS</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.100</td>
</tr>
<tr>
<td>Speed</td>
<td>2</td>
<td>0.098</td>
</tr>
<tr>
<td>Powder</td>
<td>2</td>
<td>0.196</td>
</tr>
<tr>
<td>Error</td>
<td>2</td>
<td>0.001</td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>0.394</td>
</tr>
</tbody>
</table>

Table 3. ANOVA of Grey Relational Grades. DoF: degrees of freedom, SS: sum of squares, MS: mean of squares, F: F-ratio, %: percent contribution
Discussion

Due to the difference between the number of incomplete deposits between IN625 and IN718 samples, the analysis of the IN625 data was more prone to error due to unevenness values for incomplete deposits set to three. The reasoning behind this was that the same method of obtaining unevenness could not be performed on the incomplete deposits. Additionally, although experiment 1 for IN625 was shown to be the worst deposit (least amount deposited), if measuring a difference between wall height and middle height for unevenness, experiment 1 had a significantly lower unevenness than other incomplete deposits for IN625 (experiments 6 and 8) due to a low wall height (4.58 mm) and middle height (3.15 mm), thus producing misleading data if based solely on unevenness. Figure 3 is a photo of experiments 1, 6, and 8 for Inconel 625. Therefore, grey relational coefficients for unevenness, wall height, and middle height where all considered together to determine grey relational grades (718 excluded middle height due to only one incomplete deposit) with weighting factors of 0.6, 0.05, and 0.05, respectively. The correlation of parameters in this study can be represented by a relationship between EAD and EMD [11]. By plotting EAD vs. EMD, predicting whether or not relatively even samples will be deposited becomes possible. These graphs are shown for IN625 and IN718 in Figure 4 and Figure 5, respectively. Additional research is required for confirmation and expansion of the processing window. An accurate processing window would certainly prove useful for further investigation on additively manufactured Inconel 625 and 718 samples. Consequently, incomplete deposits can be avoided all together while improving upon complete and even samples, based on the future selected areas of study, such as obtaining a desired microstructure or optimization of tensile properties.

Figure 3. Experiments 6 (left), 1 (middle), and 8 (right) for IN625

Figure 4. Inconel 625 EAD vs EMD. e: samples with $0 \leq \text{unevenness} \leq 0.6$ mm, u: samples with $0.6$ mm $\leq \text{unevenness}$, x: incomplete deposits, others: unprinted experiments using combinations of levels, optimum: optimal EAD vs EMD found from grey relational grade analysis

Figure 5. Inconel 718 EAD vs EMD. e: samples with $0 \leq \text{unevenness} \leq 0.4$ mm, u: samples with $0.4$ mm $\leq \text{unevenness}$, x: incomplete deposits, others: unprinted experiments using combinations of levels, optimum: optimal EAD vs EMD found from grey relational grade analysis
Conclusions
In this study, Inconel 625 and Inconel 718 powders were deposited using the LENS® method of additive manufacturing. Optimum processing parameters for laser power, laser speed, and powder feed rate, were determined to be 300 W, 14.8 mm/s, and 0.225 g/s, respectively for Inconel 625, and 330 W, 14.8 mm/s, and 0.18 g/s, respectively for Inconel 718. These optimal settings were determined through the use of grey relational grade analysis. Subsequently, EAD and EMD were calculated and then plotted, relating the 3 processing parameters in order to obtain a processing window for complete, even samples, and creating some groundwork to work within a viable processing window when performing future research, such as controlling grain structure utilizing LENS®.

Acknowledgments
I am grateful to the Swanson School of Engineering, the Office of Provost, my mentor Dr. Guofeng Wang, and Dr. Brian Gleeson for funding my summer research. I am also thankful to graduate student Zhenyu Liu who provided any needed assistance to complete my summer research.

References
Abstract
Alloy 625 (also Inconel 625) is a nickel-based superalloy used in high temperature, high strength applications. In this study, we investigated the oxidation behavior of porous and non-porous Alloy 625, at a temperature of 700 °C. The sample coupons were manufactured by powder bed binder jet printing, during which powder was deposited layer-by-layer and selectively joined with binder. The samples were then cured to remove excess binder (Ethylene Glycol). By sintering under vacuum atmosphere, with two different holding temperatures, 1220 °C and 1260 °C, the samples produced a porous and non-porous state, respectively. The oxidation experiment was performed at 700 °C in an air atmosphere. The samples were examined before and after oxidation by optical microscopy and scanning electron microscopy equipped with energy dispersive spectroscopy. Complex oxide scales composed of Cr₂O₃, NiCr₂O₄ and NiO formed on the surface of the oxidized porous samples; however, formation of an oxide layer on the outer surface of the non-porous samples was delayed. In fact, the rough surface and micropores of the porous samples provided fast diffusion paths for oxygen, accelerating the formation of the oxide layers. Therefore, non-porous samples, sintered at higher temperature, provide a better resistance to high temperature oxidation in air.

Keywords: Alloy 625; Powder Bed Binder Jet Printing; Oxidation; Electron microscopy observation; Elemental analysis.

Introduction
The modern world of metallurgy employs several methods for preparation of finished metal products. Additive manufacturing (AM) involves a process of joining materials to create an object from 3D model data, usually layer-by-layer, as opposed to subtractive manufacturing [1]. AM provides an opportunity to produce single parts with highly complex shapes and internal features that are either very expensive, consist of numerous parts or are impossible to produce with subtractive methods [2].

Alloy 625 is a nickel-based superalloy showing extraordinary properties including high temperature strength, toughness, and surface in high temperature corrosive or oxidative environments [3]. Good corrosion resistance results from the formation of a protective oxide scale with very low porosity, good adherence, and thermodynamic stability and slow growth rate [4]. These properties of Alloy 625 make it a desirable material for study in applications of high strength and high temperature environments.

The protective oxide scale of Alloy 625 is attributed to presence of chromium in the alloy, but the addition of ternary elements, such as iron, niobium and molybdenum, also influences oxidation behavior [5]. It is observed that formation of the Cr₂O₃ oxide film and NiO on the oxide layer can increase corrosion resistance. However, at higher temperatures (1100 °C), alloying component oxides form, e.g. from Nb and Ti, in the oxide films. The delayed oxide formation can be explained by the relative thermodynamic stabilities and diffusivities of these alloying elements, such as Nb and Ti, in the metal [5].

The focus of this study is to investigate the oxidation behavior at 700 °C of powder bed binder jet printed...
(PB-BJP) and sintered samples that used gas atomized alloy 625 powder as feedstock.

After the completion of the sintering and oxidation processes, the samples and resulting surface oxides were characterized using optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

This experiment analyzes the oxidation of Alloy 625 samples that are porous and non-porous. Non-porous materials are selected for most high strength, high temperature applications because pores are considered to be defects that reduce structural properties, especially fatigue properties; however this experiment explores the oxidation of porous samples as an option in alternative applications. Porous solids are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but throughout the bulk of the materials [6]. New frontiers exploring the function and structure of porous materials seek to utilize the specific behavior to their advantage.

**Methods**

The feedstock alloy 625 powder used for PB-BJP was produced by Ar gas atomization. The chemical composition of the powder given in Table 1 is identified via EDS and provided by the powder distributor. SEM micrographs (see Figure 1) show that the powder particles are spherical in shape.

Cubic coupons with the dimensions of 12.5 mm × 12.5 mm × 5 mm samples were printed with an ExOne M-Flex 3D printer. This PB-BJP uses an AM method in which powder is deposited layer-by-layer and selectively joined with a binder that acts like glue between the powders. Once a layer of powder was deposited onto the previous layer, the inkjet print head deposits the binder according to the desired sample model layer. The binder used for this experiment was Ethylene Glycol (Monobutyl) Ether. A heater then moved over the powder and binder to “cure” or harden the binder for this layer. After all the samples had been completely built, the entire built box was removed from the printer and additionally cured at 175 °C for 8 h in a JPW Design & Manufacturing furnace (model ST333ATUL480V9KWC).

Once removed from the curing furnace, the built box with the cured samples was carefully vacuumed to remove the powder surrounding the printed samples. The remaining coupons, referred to as “green parts,” were fragile and required further processing in a sintering procedure. Sintering attempts to compact and form dense solids by heating samples to a temperature near the melting point of the material.

Samples were then sintered in an alumina powder bed inside a Lindberg/Blue STF54434C tube furnace under vacuum using a Pfeiffer MVP 020-3 AC vacuum

| Table 1. Chemical composition of the alloy 625 powder in wt-% as provided by the manufacturer (top row) and as measured by energy dispersive x-ray spectrometry (bottom row). |
|---|---|---|---|---|---|---|---|---|---|
| Ni | Cr | Fe | Nb | Mo | Al,Ti | C | Mn | Si |
| Bal. | 21.20 | 3.09 | 3.63 | 8.91 | 0.06 | 0.03 | 0.01 | 0.01 |
| Bal. | 21.01 | 2.67 | 4.12 | 8.46 | 0.20 | 3.75 | 0.04 | 0.10 |
pump with different holding temperatures (1220 °C and 1260 °C) for 4 h. The general sintering profile was the following:

1. Heat with 5 °C/min to 600 °C, 2. Heat with 3.2 °C/min to 1000 °C, 3. Heat with 2.8 °C/min to the holding temperature (between 1220 and 1260 °C), 4. Hold for 4 h, 5. Cool with 1 °C/min to 1200 °C, 6. Cool with 3.1 °C/min to 500 °C and 6. Cool to room temperature. Figure 2 provides an illustration of the temperature profile for the sintering process.

To complete microstructural observations of the sintered coupons before oxidation, specimens were cross-sectioned, mounted, ground and polished. Samples were ground with various sandpaper grits, up to 1200-grit, followed by polishing with alumina particles to 0.05 µm. Imaging was carried out with a Keyence digital optical microscope (DOM) with a dark field Z20 lens and a multi-diffused adapter at varying magnifications.

The oxidation step was performed in a tube furnace at a temperature of 700 °C. Finally, microstructural characterizations, compositional analyses were conducted using JEOL (JSM 6510) scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectrometry (EDS).

**Results**

Figures 3 and 4 show optical and scanning electron micrographs, respectively, of the PB-BJP Alloy 625 samples sintered at (a) 1220 °C and (b) 1260 °C.
These images allow the observations of the pore structure and shape, pore size, and overall porosity. It is apparent that sintering at the higher temperature of 1260 °C results in lower porosity. The observed porosity in the samples sintered at 1220 °C and 1260 °C is 70% and 99%, respectively. For the samples sintered at 1220 °C, the pores are large and connected throughout the microstructure (Figures 3a and 4a). The samples sintered at 1260 °C demonstrate pores that are significantly smaller, spherical in shape and not connected within the microstructure (Figures 3b and 4b). Also the presence of pores at the surface of the porous samples provides a much larger total surface area in the porous samples when compared with the non-porous samples.

Figure 5 shows the SEM micrograph of the non-porous samples sintered at 1260 °C for 4 h, and oxidized at 700 °C for 12 h.

The micrographs in Figures 5a and 5b show the dark matrix of the non-porous sample and a distribution of white carbides throughout the microstructure.

Figure 6 shows the SEM micrographs of the porous samples sintered at 1220 °C for 4 h, and oxidized at 700 °C for 12 h. Figure 6 illustrates the microstructure of the porous sample at different magnifications to show the different characteristics of the microstructure.

Figures 6a and 6b show a similar dark matrix of the porous sample, but the microstructure also contains large grey oxide islands. Figure 6c magnifies these larger grey islands to show small rod-like white precipitates within the islands.

Discussion

It is evident from the OM and SEM micrographs that reduction in the quantity of pores and reduced pore size is related to the increased sintering temperature. The different temperatures for sintering allow us to investigate the behavior of porous and non-porous samples of Alloy 625 in high-temperature oxidation environments.

As seen in Figures 3 and 4, internal and surface porosity are very different between the samples sintered at...
1220 °C and 1260 °C with porosities of 70% and 99%, respectively. The implication of larger surface area is that there are more faces on the porous samples that are exposed to the air atmosphere, providing more areas for reactions to occur, and oxide scales to build.

When comparing Figures 5 and 6, it is evident that the oxidation behavior is very different and much increased in the case of the porous coupon. This disparity between the appearances of the oxide scales of the samples is due to the dramatically increased surface area in the porous sample (1220 °C) compared to the surface area of the non-porous sample (1260 °C). Furthermore, the oxide scales on the porous surface appear in form of grey islands with submicron crystals, indicating a different composition between the oxide scales formed on the porous and nonporous samples. EDS analysis indicates that the oxide scale is made of NiO (rod-like oxide in Figure 6c) and NiCr₂O₄ (grey islands in Figure 6a and 6b) [7]. Additionally, the white crystals are determined to be NbC, (big crystals in Figure 5a) formed in the grain boundaries due to aging and Ni₃Nb in the bulk grains (small precipitates in Figure 5a and 5b). It is determined that the oxidation resistance is higher in the non-porous sample as evidenced by the formation of the thin spinel structure and Cr₂O₃ in addition to submicron precipitates in the grain boundaries and bulk grains. Thus, denser samples provide not only a proper microstructure for most mechanical applications, but they also showed better oxidation resistance in high temperature environments; however further exploration of the behavior of porous Alloy 625 may prove useful in applications requiring specific reactions with atoms or ions in atmosphere.

Conclusions
It is evident from the Optical Microscopy and Scanning Electron micrographs that the reduction in the quantity of pores and shrinkage in the pore size is related to the increased sintering temperature of the 3D printed coupons. In addition to the effect of the sintering temperature on the porosity of the samples, it is determined that the increased surface area in porous samples provides more locations for the development of oxide scales. The rough surface and micropores of the porous samples provide faster diffusion paths for oxygen, accelerating the formation of the oxide layers. The numerous oxide scales formed on the samples include various nickel oxides, NbC and Cr₂O₃, indicating reactions with oxygen from the atmosphere, the nickel base of the material and micro-alloying elements present within the material. When making conclusions concerning oxidation behavior and the needs of industry, it is evident that the non-porous samples of Alloy 625 perform more efficiently within a high intensity environment. The fully dense samples provide a properly sintered microstructure and demonstrate better resistance to oxidation in high temperature applications.

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References
Effect of Variation of Geometric Properties of Bamboo on Culm Buckling

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Abstract
Characterized by its high strength-to-weight ratio and recognition as one of the most renewable resources on Earth, bamboo has reached the forefront of research among non-conventional construction materials. However, the innate functionality of its geometric and material properties makes direct application of Euler’s buckling equation produce unreliable results. This paper thoroughly documents the geometric variation and single culm, buckling capacity of two common species utilized in construction, p. Pubescens (Moso) and b. Stenostachya (Tre Gai). Our investigation consisted of measuring the sectional properties of eight Moso culms, four of which were chosen for additional buckling testing. A linear, best fit analysis performed on the geometric data, as well as data compiled from a previous study on Tre Gai, showed that both species exhibit a decrease in their area and moment of inertia along the length of their culm. Most significantly, Moso, a thin-walled species, experienced a decrease in its radius of gyration, whereas Tre Gai, a thick-walled species, experienced an increase. By following Euler’s critical buckling stress equation (Eq. 2), it was observed that Tre Gai’s increase in radius of gyration allowed for a greater stress in its columns, marginally offsetting the geometric taper along its height which otherwise would have greatly reduced its capacity. Future studies, coupled with the consideration of material property variation, are paramount for bamboo to be accepted as a viable construction material.

Keywords: bamboo, column buckling, functionally graded material, non-conventional construction material

Introduction
There is a desire to find less expensive, safer, and more sustainable construction materials. While the application of conventional materials such as steel and concrete will continue to be optimized, there has been a recent increase in the exploration of utilizing non-conventional construction materials. Bamboo, a naturally abundant, renewable material is currently being investigated worldwide. A key incentive for this pursuit is the notion that it can help reduce extraneous costs and harmful emissions that otherwise accompany steel and concrete. Bamboo is already used extensively throughout India and Asia for housing and footbridges, where its high strength-to-weight ratio and flexibility makes it an attractive candidate for construction in intense seismic regions. However, bamboo is commonly considered a non-engineered material and its application is primarily based on vernacular custom rather than the mechanical principles of structural design. The innate functionality of bamboo’s geometric and material properties is the basis of this custom. This study is part of a larger effort to further understanding of the material and bring bamboo acceptance as an engineering material [1].

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Bamboo as a Functionally Graded Material

Bamboo is a functionally graded material (FGM). FGMs are characterized by variation in material and/or geometric properties. In bamboo, this is characterized with respect to the principle axes of the material. Bamboo exhibits both geometric and material variation across its structure. In order to help reduce self-weight and resist wind loads, the diameter and thickness of a bamboo culm generally tapers along its height. This phenomenon has two effects. First, it helps reduce the weight of the stalk, or the culm, and secondly it results in a flexural stiffness proportional to the lateral wind-induced moments. Bamboo’s material properties also vary within a cross section, in the radial direction. The fiber (cellulose) content increases from the interior wall of the culm outward. This places more fibers near the outer culm wall where it will better resist bending from wind induced loads. The fiber volume also varies along the culm height; as the culm wall area decreases with height, the volumetric distribution of the fibers increases resulting in a more uniform sectional stiffness (product of Young’s modulus and moment of inertia, EI) than predicted by geometry alone [2].

This paper describes the geometric variation of culms from two bamboo species commonly used in construction: a thin-walled species, p. Pubescens (Moso), and a thick-walled species, b. Stenostachya (Tre Gai). From this, an understanding of the differences of geometric variability between thick and thin-walled species of bamboo is achieved. Additionally, the effect of the geometric variability between thick and thin-walled species on their respective buckling behavior of single culm bamboo columns is studied.

Methods - Assessing Geometric Variability

As a continuation of a previous study [2] on the thick-walled Tre Gai species, a similar study of the dimensional variability of a thin-walled Moso was carried out. Four culms, approximately 2600 mm long, were selected for their superior straightness, minimal defects and variation in diameter over their length. Large and small diameter specimens were selected to determine if specimen diameter needs to be considered separately or may be a basis for normalization. An additional four culms left over from the previous study were also used to obtain geometric variation (but not used for subsequent compression testing). A specialized jig was used to obtain the diameter ($D_n$) and length of each internode ($L_n$), and the initial out-of-straightness at the middle of each internode. A detailed description of the measurement procedure is presented in [2].

The wall thickness at each quadrant was measured after testing when the culm was cut. Due to the unsymmetrical behavior of bamboo, the average values of the diameter and wall thickness along the N-S and E-W axes, and N, S, E, and W locations, respectively, were obtained [2]. Cutoffs were later used to establish compression modulus of the bamboo, using the method of the ISO standard [3].

In order to analyze the geometric variation across all culms, geometric properties were normalized with respect to the values at the base of the culm (i.e., typically the location of the largest diameter). Culm diameter ($D_1$), wall thickness ($t_n$), cross sectional area ($A_n$), moment of inertia ($I_n$) and radius of gyration ($r_n$) at each internode, $n$, were considered and presented in terms of normalized length ($L/D_1$) where $D_1$ is the diameter of the culm at the first internode. Linear best fit analyses were then conducted to establish trends in section geometry along the culm length.

Methods - Axial Compression/Buckling Tests

Four Moso culms were selected for single culm buckling tests. Culms were cut to length, approximately 2400 mm, and end plates with neoprene padding were attached. The culms were tested in concentric uniaxial compression in a servo-hydraulic controlled universal testing machine (UTM) where their critical load and corresponding axial and lateral displacements were measured. Lateral displacements were obtained using horizontally-oriented, draw wire displacement transducers (DWT) attached at $L/3$, $L/2$, and $2L/3$, where $L$ is the height of the culm. Photos taken during the experiment were later analyzed in Adobe Photoshop to determine lateral deflection at each
Deflections at the following three load states were determined in this manner: zero loaded culm, critical buckling load, and final load attained. Additionally, all specimens were tested in their natural orientation; i.e., with the largest cross section at the bottom, and roller support conditions were provided to enforce the direction of buckling.

This testing set up can be seen in Figures 1 and 2 where culms were equipped with a 25.4 mm thick steel end plates and centered using a 12.7 mm diameter bolt aligned with the center of the end internodes. Between the plate and the culm, a 3.2 mm thick neoprene pad was inserted to help ensure more uniform bearing and to reduce the likelihood of a local bearing failure. The end plate assembly is embedded in the internode using plaster of Paris. This helps to maintain the concentric loading geometry and provides some safety against the end of the culm ‘kicking’ out during a test. Finally, to mitigate the possibility of compression load-induced splitting, a pipe clamp is installed around the culm at its ends.

Results

It was found that there existed no significant difference in normalized property variation based on large and small diameter Moso specimens. Yet, there does exist a clear distinction between the geometric variability of the thick and thin-walled bamboo species. Both species exhibited a reduction in both culm diameter and wall thickness with height resulting in a reduction in area and moment of inertia. However, Tre Gai exhibits only a marginal reduction in diameter resulting in a different relationship between area and moment of inertia. As shown in Figure 3, the radius of gyration of the thick-walled Tre Gai species increases with height along the culm, whereas in Figure 4, it decreases for the thin-walled Moso.

The summary of deflected shapes is shown in Figure 5 and applied axial load versus lateral displacement plots for the thin-walled culm tests are presented in Figure 6. Table 1 provides a summary of the experimental and predicted values for buckling capacities.

![Figure 1. Photograph of end condition](image)

![Figure 2. Schematic drawing of end condition](image)
were derived using averages of the moment of inertia along the entire length, and average Young’s modulus found at mid height of the culm. It was found that the average Young’s modulus for the Moso specimens was 6,645 MPa (COV = 0.08). The average Young’s modulus for Tre Gai was taken as 13,450 MPa (COV = 0.32) [2]. The moisture content for Moso was additionally found to be 12.2% and for Tre Gai it can be assumed to be within this vicinity as well.

**Discussion**

As previously noted, the geometric variation between bamboo species is apparent. While additional testing is planned, the results from this pilot study provide clear evidence of differences in axial load resisting behavior. The thick-walled species exhibits a nearly constant diameter and slight increase in radius of gyration along its height. While on the contrary, the thin-walled species experiences a decrease in both diameter and radius of gyration along its height. This geometry affects the culm global buckling behavior and the ‘effective’ geometric values used to predict this capacity.
With this in mind, there exists a noticeable effect on the column buckling behavior of single-culm columns. In Figure 6, it can be seen that the upper third point (0.66L) of the culm experiences greater lateral deflections, after the critical buckling load is reached, than the lower third point (0.33L). Additionally, it can be seen in Figure 5 that the greatest lateral deflection appears to occur slightly above mid height of the culm. Thus if the column were to be reinforced to reduce deflection, it should occur here, rather than the more conventional location of mid height. Though not taken into account in this study, it is interesting to recall that Young’s modulus and the uniformity of sectional stiffness of the cross-section will increase along the height of the culm, theoretically helping to offset the reduction in section geometry that occurs with height along the culm.

Using the Southwell method [4], the critical buckling load was found as the slope of δ versus δ/P curve plotted for the prebuckled column in which P is the applied load and δ is the lateral displacement at the mid height of the culm obtained from the DWT data. The intercept of this slope with the δ axis provides an estimate of the initial imperfection of the column along its length. It was found that the Southwell method captured the apparent buckling load very well but did not capture the initial imperfection. The latter is believed to arise because the Southwell approximation is based on a homogenous prismatic column having an initial shape that may defined by a sine function; this is not the case for the bamboo culms tested. Predicted values for the buckling capacity were calculated based on Eq. 1 and Eq. 2, using the aforementioned data for Young’s modulus. It was found that there appears to exist no distinct trend in the relationship of the predicted versus experimental values for buckling capacity of the thick and thin-walled species when they were observed either separately or together. As a result, it can be concluded that the geometric variability of

![Figure 6. Applied axial load versus displacement results for Moso, culm C4](image)

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<tr>
<th>Test ID</th>
<th>Length</th>
<th>A_{shl} (mm$^2$)</th>
<th>L_{shl} (mm)</th>
<th>Slenderness (KL/t)</th>
<th>Critical Load P_{cr} (kN)</th>
<th>Critical Stress $\sigma_{cr}^a$ (MPa)</th>
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<th>Slenderness (KL/t)</th>
<th>Critical Load P_{cr} (kN)</th>
<th>Critical Stress $\sigma_{cr}^a$ (MPa)</th>
<th>Critical Load P_{cr} (Equ. 2) (kN)</th>
<th>$P_{cr}/P_{cr}$</th>
</tr>
</thead>
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<tr>
<td>C1</td>
<td>2600</td>
<td>3,400</td>
<td>2,440,000</td>
<td>53</td>
<td>52</td>
<td>47.3</td>
<td>158.4</td>
<td>0.305</td>
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<td></td>
<td></td>
<td>3,500</td>
<td>2,461,000</td>
<td>54</td>
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<td>46.3</td>
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<tr>
<td>C2</td>
<td>2600</td>
<td>3,400</td>
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<td>50</td>
<td>43.6</td>
<td>148.2</td>
<td>2.96</td>
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<td></td>
<td></td>
<td>3,000</td>
<td>2,049,000</td>
<td>55</td>
<td></td>
<td>43.2</td>
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<tr>
<td>C3</td>
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<td>3,800</td>
<td>2,521,000</td>
<td>56</td>
<td>96</td>
<td>42.3</td>
<td>164.9</td>
<td>1.72</td>
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<td></td>
<td></td>
<td>3,700</td>
<td>2,550,000</td>
<td>55</td>
<td></td>
<td>44.6</td>
<td>166.8</td>
<td>1.74</td>
</tr>
<tr>
<td>C4</td>
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<td>3,600</td>
<td>2,263,000</td>
<td>57</td>
<td>63</td>
<td>42.2</td>
<td>146.9</td>
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<td></td>
<td></td>
<td>3,500</td>
<td>2,258,000</td>
<td>56</td>
<td></td>
<td>42.2</td>
<td>146.6</td>
<td>2.33</td>
</tr>
</tbody>
</table>

*Denotes predicted values

Table 1. Buckling capacities for Moso and TreGai columns
bamboo columns does produce a significant effect on the accuracy of predicting their buckling capacity, particularly in the thin-walled species studied here. The development of a procedure to address this variation is paramount if bamboo is to be accepted as a conventional, construction material.

Conclusions

In this study, the geometric variation of culms from two bamboo species commonly used in practice: a thin-walled species, *p. Pubescens* (Moso), and a thick-walled species, *b. Stenostachya* (Tre Gai) was presented. Both species exhibit a reduction in both culm diameter and wall thickness with height resulting in a reduction in culm area and moment of inertia. However, the relationship between these reductions is markedly different. In the thin-wall species, the resulting radius of gyration falls, as is typical in a classical 'tapered' element. However, in the thick-wall species, the radius of gyration increases with height suggesting greater critical buckling stress (Eq. 2) along the height of the column, offsetting, to some degree, the effects of geometric taper. Further study on this issue is required since it also is known that the modulus of elasticity tends to increase along the height of the culm (as well as vary radially in the cross section).

Four axial load tests of single Moso culms were performed; results were comparable to earlier tests of the Tre Gai. These data will provide benchmark tests for a future analytic program investigating the effects of varying geometry and material properties in the culm section and along the culm.

Acknowledgments

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References


Appendix

\[ P_{cr} = \pi^2 EI/(KL)^2 \]  

Eq. 1  

Where: \( P_{cr} \) is the critical buckling load, \( E \) is Young’s modulus, \( I \) is the moment of inertia, \( K \) is an effective length coefficient and \( L \) is the length of the column.

\[ \sigma_{cr} = \pi^2 E/(KLr)^2 \]  

Eq. 2  

Where \( r \) is the radius of gyration of the section.
Responses of Hybrid Masonry Structures in 1994 Northridge Earthquake Simulated Using Finite Element Analysis Program

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Abstract
Hybrid masonry is a relatively new structural system that consists of reinforced concrete masonry wall, steel frames, and steel connectors. This study focuses on how various Type I hybrid masonry structures react to the 1994 Northridge Earthquake. Numerical data was obtained through large-scale experiments of hybrid masonry structures conducted at the University of Illinois Urbana-Champaign. This data was then used to configure Finite Element Analysis Program (FEAP) models of various Type I hybrid masonry structures to explore which designs would optimize energy dissipation. After each successful simulation, a final damage picture was produced along with output files detailing the behavior of several components of the system subject to the earthquake loading. Based on the damage pictures and the properties of steel, it was determined that structures with smaller connectors contribute less damage to the masonry panel, but more deflection to the connectors. Connectors that absorb most of the seismic deformation protect the masonry panel and steel frame from undesired damage. Thus, restoration of the structure after a seismic event can be made easier by simply replacing the connectors.

Keywords: hybrid masonry, seismic, connectors, finite element analysis

Introduction
Hybrid masonry wall consists of masonry wall attached to surrounding steel frame by steel connectors. The hybrid masonry system was first proposed in 2006 to offer a design alternative to the construction of frame buildings with masonry infill, and to provide sturdy, yet flexible, buildings that could be most beneficial to seismic areas [1]. Technologies like hybrid masonry have surfaced as means to accommodate for design requirements in moderate to high seismic areas [2]. Hybrid masonry structures benefit seismic areas because they provide great ductility, stiffness, and strength that allow them to withstand intense inelastic deformation while keeping their overall strength capacity. Hybrid masonry structures have only been introduced in low seismic zones. This is because adequate testing is needed in order to examine the applicability of this system in areas of higher seismic activity before implementation. This work aims to demonstrate that it is practical to use these structures in moderate to high seismic regions as well. It is part of a larger study to find the optimal design of hybrid masonry structure that can act as a new lateral-force-resisting system in areas of high seismic activity [3]. The purpose of this study is to determine the relationship between connector width and the overall damage to the Type I hybrid masonry system. This was accomplished by developing finite element analysis models using results from experiments conducted at the University of Illinois Urbana-Champaign. This is the first study that examines how various Type I hybrid masonry structures react to the 1994 Northridge Earthquake which occurred in the highly seismic region of Los Angeles, California.

Background
Type I hybrid masonry (shown in Figure 1) has gaps between the masonry panel and the frame on all sides. Therefore, gaps exist on both sides (allowing lateral drift) as well as on top (allowing vertical deflection) of
the masonry panel. The gap between the masonry wall and the steel frame precludes axial load and in-plane shear stress at the steel columns from being transferred from the frame to the panel [2]. The masonry panel makes only indirect contact with the frame through the steel connectors within these gaps. The steel connectors used in hybrid masonry panels can be either rigid link plates or ductile fuse plates. In Type I hybrid masonry, steel connectors transfer in-plane shear, but not vertical load, between the steel frame and the top of the masonry panel. Here, the framing supports all of the weight of the masonry wall, including gravity loads [3]. Headed studs are used to transfer shear between the frame and the masonry [4].

Other work on the relationship between connector size and hybrid masonry systems was performed by Ozaki-Train, Mitsuyuki, and Goodnight [5, 6, 7] at the University of Hawaii at Manoa. Their works thoroughly examined different connector plates and suggested the optimal connector plate sizes used for large-scale hybrid masonry testing at the University of Illinois Urbana-Champaign [8]. This work builds on this existing research as it uses calibrated parameters from previous works in order to formulate a test for the optimal connector sizes to use in present-day hybrid masonry construction using a unique computational damage model. Using continuum damage mechanics, a two-dimensional, nonlocal, two-scalar damage model is developed for the masonry panel, and a two-dimensional frame element based on the elastoplastic model accessible in FEAP is used to model the steel connectors and steel beams [9]. Given this technique, a great way to test for the optimal connector plate to implement in moderate to high seismic zones is through simulations of hybrid masonry structures (of Type I) subject to loadings from the 1994 Northridge Earthquake. This earthquake was chosen because it is considered one of the most costly natural disasters in the U.S, with damages estimated at around $20 billion [10].

Methods
The data used to model behavior of hybrid masonry structures was obtained from both the University of Hawaii at Manoa (UHM) and the University of Illinois Urbana-Champaign (UIUC). Experiments conducted at both universities were part of a larger project aimed at studying the suitability of hybrid masonry structures in moderate to high seismic regions [2]. At UHM, thorough, small-scale testing of connector behavior in Type I masonry systems were conducted. These UHM experiments were previously replicated at Rice University using FEAP for calibration of damage models [2]. Large-scale experiments of two-story hybrid masonry structures were conducted in the Network for Earthquake Engineering Simulation/Multi-Axial Scale Sub-Structured Testing & Simulation (NEES MUST-SIM) facility at the UIUC [8]. The structures tested at UIUC looked similar to that shown in Figure 1. The purpose of these large-scale experiments was to demonstrate the efficiency of hybrid masonry in withstanding seismic loads. The tests incorporated various connection methods between the masonry and the steel frames in order to examine the outcomes on tremulous behavior. Both energy dissipating fuses and link plates were created to transfer forces from the steel to the masonry panels. These structures were subject to cyclic and monotonic loading in order to mimic the effects of an arbitrary earthquake. Based on the force distribution of the hybrid masonry structure, the worst possible loading combination for the steel frame was chosen for the testing. The magnitudes of the applied vertical and lateral loading was based on this loading combination,
and the applied moments on the beam were factors of the lateral force, number of connector plates, and the distance to the connector bolt from the centerline of the beam. Experimental data for the UIUC tests can be found at http://nees.org/warehouse/project/917. The preliminary results from the tests run at the NEES MUST-SIM facility show that hybrid masonry is a practical option for seismic regions. [1].

The conglomerated numerical data from UIUC was sent to the computational mechanics laboratory at Rice University and used to configure damage models for hybrid masonry systems (similar to those from the full-scale tests) on FEAP. The major challenge to the hybrid masonry system simulation is the ability to accurately model damage mechanisms of the structures. The modeling framework in this study utilizes a typical plasticity model with hardening for the steel components and a nonlocal, two-scalar damage model that encompasses the tensile and compressive behavior of the masonry panel [2]. In this case, the nonlocal approach is preferred because it avoids the pathological sensitivity to mesh size (stress locking that causes damage to be confined to a relatively small volume of material) that occurs when using the local approach. Modeling the steel components is straightforward because there is a two-dimensional frame element available in FEAP that models steel beams based on the elasto-plastic concept. The concrete masonry units (CMUs) used in hybrid masonry walls have dimensions of 8in x 8in x 16in, making them homogenous. Thus, a homogenization approach is used to conduct a non-linear analysis of large and complex structures. In the two-scalar, two-dimensional nonlocal continuum damage model, the masonry wall is taken as a homogenous mixture and the reinforcements are treated as separate constituents. The framework consists of a mesh of square-shaped nodes which represent various points on the real structure. The model for the masonry panels exists as two-dimensional, four node quadrilateral elements with 2x2 Gauss points. One large quadrilateral is positioned slightly above the other (representing the bottom and top floor masonry panels). The two connectors are represented by two nodes, and the steel beams are represented as nodes along a line. The simulation uses a non-local approach where stress at one point depends on the state of the entire body [9]. This approach enables mesh size to vary, thus avoiding pathological sensitivity. There are 2001 loading steps and each step varies between 10^{-5} and 10^{-24} seconds. The finite element model takes into account the steel frame, the masonry wall, the panel reinforcements, and the connectors. The steel frame is pinned at the base of the columns, while the masonry is fixed at the base. The connectors are fixed at the upper portion of the frame and secured horizontally to the lower portion of the masonry panel. The two materials utilized are steel and masonry. The properties for both the steel components and the masonry panel are shown in Table 1 and Table 2 respectively. \( v \) is Poisson’s ratio, \( \beta \), is a delay constant that determines the speed at which

<table>
<thead>
<tr>
<th>Yield stress (N/m²)</th>
<th>Ultimate stress (N/m²)</th>
<th>Young’s modulus (N/m²)</th>
<th>( v )</th>
<th>( \beta_s )</th>
<th>( H_{iso} )</th>
<th>( H_{kin} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5.07 \times 10^8 )</td>
<td>( 8.07 \times 10^8 )</td>
<td>( 2.09 \times 10^{11} )</td>
<td>0.3</td>
<td>45</td>
<td>0</td>
<td>( 1.2 \times 10^8 )</td>
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</table>

<table>
<thead>
<tr>
<th>( E_m ) (N/m²)</th>
<th>( \nu )</th>
<th>( f_c ) (N/m²)</th>
<th>( A_c )</th>
<th>( B_c )</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon_f )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.1 \times 10^9 )</td>
<td>0.2</td>
<td>( 22.3 \times 10^6 )</td>
<td>1.065</td>
<td>101.721</td>
<td>0.0006</td>
<td>0.004</td>
<td>1.14</td>
</tr>
</tbody>
</table>
the material shifts from elasticity to plasticity, $H_{iso}$ is the isotropic hardening modulus, $H_{kin}$ is the kinematic hardening modulus, $E_m$ is the modulus of elasticity for masonry, $f_c$ is the compressive strength of concrete, $A_c$ and $B_c$ are both parameters with no direct physical meaning, $\varepsilon_0$ is the initial damage threshold, $\varepsilon_f$ is the parameter influencing the post-peak slope of the stress strain curve for uniaxial tension, and $\beta$ is used to diminish the impact of damage under shear force [2]. Force values in this study are input values for loadings felt by the 1994 Northridge Earthquake. The earthquake data was obtained from the University of California, Berkley at http://peer.berkeley.edu/ngawest2/databases/. Variables for all components of the simulations except for the connector widths were held constant; including loading applied, location of loading, masonry wall, hybrid masonry type, steel beams, etc.

Data Processing
The FEAP simulation applied the earthquake loadings to the two dimensional mesh figures and recorded them in time steps. During the simulations, some structures converged (failed) early in the simulation before all of the earthquake loading steps could be applied. In these cases, the simulations required re-runs. The acceleration time history for the Northridge earthquake with time increments of .02 seconds can be found at http://kouzou.cc.kogakuin.ac.jp/Open/Green/Northridge/data/PEER/TAR090.AT2.txt.

Results
Walls were simulated with connectors of the following widths: 38.1 mm, 50.8 mm, 63.5 mm, 76.2 mm, 81.28 mm, 86.36 mm, 88.9 mm, 91.44 mm, 96.52 mm, 101.6 mm, 114.3 mm, 127 mm, 139.7 mm, 152.4 mm, 165.1 mm, and 177.8 mm. After each successful simulation, a final damage picture was produced. The intensity of damage done by the earthquake was represented using a color scale. Blue indicates no damage while red indicates fully damaged. Output files were also produced and provided different characteristics regarding each structure’s reaction to the earthquake loadings. These

![Figure 2. Damage distribution for Type I hybrid masonry wall subject to earthquake loading with 127 mm connectors (3(a)) and 139.7 mm connectors (3(b)). Deep blue ($\omega=0$) indicates no damage while deep red ($\omega=1$) indicates severe damage.](image)
Undergraduate Research at the Swanson School of Engineering

Ingenium 2016

output files were used to extract data at specific nodes to be used for further study. The damage figures give unique results for each connector size examined, and there appears to be a relationship between the size of the connector and the overall damage to the wall. For example, the damage distributions of the 127 mm and 139.7 mm connectors (Figure 2(a) and 2(b) respectively) show that the wider connector (139.7 mm) resulted in more damage to the masonry wall compared to the thinner connector (127 mm). Damage to the connectors is represented by the small red areas located near the top of the first floor on the 2-D damage model (See Figure 2). Also, compared to the overall damage of the wall with the 127 mm connector, the damage figure indicates failure of both connectors (indicated by the deep red color, $\omega=1$), but also shows parts of the masonry with no damage at all. Both walls with 127 mm and 139.7 mm connectors show severe damage to the connectors, but the wall with the 139.7 mm connector shows complete damage and failure of the first floor. Damage to the connectors and to the masonry wall will be defined by the damage variable, $\omega$. As shown in Table 3, a $\omega$ value of 0 represents an undamaged material while a $\omega$ value of 1 represents a fully damaged material. In this case, damage is defined as the overall deformation at each load step.

**Discussion**

The connector width appears to have an effect on the severity of the damage done to the masonry panel. Since a weaker connector (one of a smaller width) is more ductile than a stronger connector (one of a larger width), structures with smaller connectors tend to show less damage done to the masonry panel compared to damage done to the connectors. On the other hand, structures with larger connector widths tend to show more damage done to the masonry panel compared to damage done to the connectors. Connectors seem to deflect before failure, indicated by relatively less damage to the masonry wall. Deflection in connectors cannot be well represented in the figures above as they only indicate damage to the system. Although deflection is not shown in the damage figures, based on the presence of only two materials in the hybrid masonry structure (steel and masonry), it is safe to assume that energy not dissipated by the masonry wall is dissipated by either the steel connectors or by the steel frame. Since the input parameters for all components but the steel connectors were held constant, any change in the damage figure can be taken as a direct result from the change in the connector width. Energy dissipated by the connector is represented by deflection until its failure.

**Conclusions**

Hybrid masonry offers great benefits to framed construction, such as increased lateral stiffness, refined redundancy, better construction of masonry within the frame, and increased chances for reduced construction costs [1]. Since the smaller connectors in this study gave rise to relatively less damage to the masonry panel, it may be beneficial to use connectors with widths of 38.1 mm, 50.8 mm, or 63.5 mm in hybrid masonry construction today. After an earthquake, severe damage to the hybrid masonry structures can be costly. Therefore, by preventing extensive damage to the masonry panel, costs are reduced to only having to restore sections of masonry and/or replacing steel connectors. Steel beams may also have to be replaced if the connectors fail to transfer load to the masonry effectively, or if the loading in the beam exceeds its yielding stress. Ultimately, hybrid masonry structures benefit the public by preventing higher degrees of structural damage and casualty that would normally result from a catastrophic seismic event.

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**Table 3.** Highest recorded damage variable ($\omega$) for masonry panels and steel connectors based on the corresponding connector width in the hybrid masonry system.

<table>
<thead>
<tr>
<th>Connector width (mm)</th>
<th>38.1</th>
<th>50.8</th>
<th>63.5</th>
<th>76.2</th>
<th>81.28</th>
<th>86.36</th>
<th>88.9</th>
<th>91.44</th>
<th>96.52</th>
<th>101.6</th>
<th>114.3</th>
<th>127</th>
<th>139.7</th>
<th>152.4</th>
<th>165.1</th>
<th>177.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masonry damage ($\omega$)</td>
<td>0.0</td>
<td>0.4</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Connector damage ($\omega$)</td>
<td>0.0</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>1.0</td>
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<td>1.0</td>
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<td>1.0</td>
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Acknowledgments
Special thanks to the University of Pittsburgh and Rice University for such a wonderful summer research opportunity. Additional thanks goes to Nathan Beck for helping with editing. Funding was provided by the Swanson School of Engineering and the Office of Provost.

References
Mechanics of Anesthetic Needle Penetration into Human Sciatic Nerve

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Abstract
Painless surgery requires the injection of a local anesthetic in close proximity to peripheral nerves, such as the sciatic nerve (SN) located in the lower back. Within the SN, two connective tissue linings encapsulate the nerve bundles: the epineurium and the overlying paraneural sheath. Maximizing the anesthetic’s effect requires dose administration into the area between the sheath and epineurium. Understanding the forces required to puncture the isolated paraneural sheath (IPS), isolated nerve (IN) and nerve with paraneural sheath (NPS) is paramount for accurate anesthetic delivery. Six cadaveric SN were harvested and three specimens were dissected from each: IPS, IN & NPS. Tissue puncturing was performed with a 21Gx4-inch needle and puncture force was measured via an ASTM micro-indentation system. The average penetration force for the IPS (123±17 mN, n=6) was significantly lower (p<0.05) than the average penetration force for the IN (1047±97 mN, n=5) and the NPS (1440±161 mN, n=5). In contrast, the puncture force between the IN and NPS was not significantly different (p=0.3). Since the force to penetrate the epineurium is nearly tenfold higher than the force to penetrate the paraneural sheath, the use of low needle penetration force may be ideal for anesthetic administration.

Keywords: Sciatic Nerve, Anesthesia, Needle Mechanics, Puncture Force

Introduction
A main strategy used by anesthesiologists to control post-operative pain is the injection of local anesthetic agents in close proximity to peripheral nerves. This procedure, commonly referred to as a nerve block, is of benefit to patients who must undergo procedures, such as ACL repair surgery or sciatica pain relief [1]. A routinely targeted nerve to diminish patient’s sensation of pain when undergoing lower extremity procedures is the sciatic nerve (SN).

The SN, comprised of the tibial nerve (TN) and common peroneal nerve (CPN), is unique with respect to the fact that it is surrounded by a connective tissue sheath, known as the paraneural sheath (Figure 1). To optimize onset and effectiveness of the nerve block, the dose should be administered into the area between the paraneural sheath and the epineurium of the nerves. However, this space is limited in size, and there exists the possibility of the needle impacting the underlying nerve, which may lead to nerve injury [3-4].

The puncture force necessary to penetrate the paraneural

Figure 1. Histological image of the sciatic nerve. The nerve bundles, highlighted in pink, represent the TN and CPN. A connective tissue sheath, known as the paraneural sheath, holds both nerves together and is highlighted in yellow. The epineurium, a connective tissue lining the TN and CPN individually, is highlighted in the image with green fill surrounding the nerve bundles [2].
sheath, the epineurium of the nerve, and the nerve with overlying paraneural sheath has not been investigated. We believe that understanding the relationships of these forces will allow anesthesiologists to more accurately and safely perform sciatic nerve block. The purpose of this work is to measure the penetration force for the paraneural sheath, isolated nerve, and nerve with overlying paraneural sheath in an effort to aid anesthesiologists in the optimization of sciatic nerve blocks.

**Methods**

Seven human cadaveric sciatic nerves were harvested and stored in saline at 4°C. Three specimens were dissected from each nerve: 1. Isolated paraneural sheath (IPS), 2. Isolated nerve (IN), and 3. Nerve with overlying paraneural sheath (NPS).

**Paraneural Sheath Isolation**

Paraneural sheath isolation was performed by inserting scissors beneath the sheath and cutting down the midline of the sheath. The sheath was then detached from the underlying nerve via blunt dissection.

**Needle Penetration**

Specimens were stretched onto the mounting stage of an ASTM standard calibrated micro indentation system and secured to the area using sutures (Figure 2). Testing of the IPS was performed with a 50g load cell, as it was determined to be sufficient to capture the puncture force. A 500g load cell was used to test the IN and NPS as the 50g load cell did not allow for proper recording of the puncture force. Testing was performed using a Stimuplex A 21Gx4-inch nerve-block needle, a commonly used needle in sciatic nerve blocks. The needle was replaced after each nerve was tested to compensate for dullness that may occur due to repeated use. To simulate careful insertion of the needle, the needle was driven at a speed of 0.1 mm/sec into the specimen. After the initial puncture was made, the indenter was retracted and then the insertion-retraction of the needle was performed two more times in the same location. Data from three insertions in the same location was gathered in order to determine if a successful puncture was made during the first insertion via the calculation of the energy released per insertion. For each specimen, three different locations of at least 5 mm apart on the tissue were chosen as potential puncture sites in order to maximize the amount of puncture force data gathered for each specimen. For the IPS, six unique specimens were used and for the IN and NPS, five unique specimens were used. Each of the specimens was punctured at three different locations. The needle tip force and displacement data was continuously recorded using LabView software and calculation of puncture force and energy released during each insertion was performed in Matlab.

![Figure 2. Micro-Indentation system & mounted IN specimen. The micro-indentation system (A) contains a stepper motor (i) that is controlled by the user via LabView software. The motor delivers its impulses to the micrometer (ii) which is able to convert rotational motion to translational motion, allowing for the advancement of the needle (iii). Mounted intact nerve specimen, secured by sutures (B).](image-url)
Data Processing

Puncture Force
The needle tip force data was characterized by an increase in force up to a maximum value and then a decrease in force after the needle was retracted from the tissue. The maximum needle-tip force during the first insertion was identified as the puncture event and the force was noted. An average of the force over the three locations was calculated and this average was used to represent the force required to puncture the specific portion (IN, NPS, or IPS) of the nerve being tested. This puncture force was then averaged over the number of nerves tested.

Energy Released per Insertion
To verify a puncture was made during the first insertion, the energy released was calculated for each insertion made into the tissue for each location. Calculation of energy released was performed by approximating the area under the force displacement curve via the trapezoidal rule. The energy was averaged in a similar manner to the averaging of the puncture force.

Statistical Analysis
Statistical analysis of the puncture forces for each tissue type was performed using a paired t-test (p<0.05) to determine whether the difference in puncture force for each tissue type was significant within specimens. An unpaired t-test (p<0.05) was performed between the first and second insertion energy, as well as between the first and third insertion energy for the IPS, IN, and NPS, to determine whether a puncturing event had occurred.

Results

Needle Force-Displacement Data
The needle force-displacement data were graphed and loading and unloading curves of the needle were identified in each data set. The loading and unloading curves were deemed representative of the insertion and retraction of the needle (Fig. 3). The large singular force spike toward the end of the unloading curve was attributed to the needle tip impacting the slide.

Figure 3. Representative force-displacement curves for the IPS (A), IN (B) and NPS (C) tissues. Each curve is characterized by a loading curve (i) and unloading curve (ii) that is representative of the force experienced by the needle tip as it is being inserted and retracted, respectively. An additional force spike (iii), due to impact of the slide with the needle tip, was also observed. The puncture force was identified to occur during the first insertion and circled in each graph.
Figure 4. Needle tip puncture force (mN) for the IPS, IN and NPS (mean ± SEM). Data was averaged over the total number of nerves tested. Paired t-test, p<0.05

Table 1. Energy released (μJ) during each insertion for the IPS, IN and NPS (mean ± SEM).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Energy Released (μJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First Insertion</td>
</tr>
<tr>
<td>IPS</td>
<td>131±28 (n=5)</td>
</tr>
<tr>
<td>IN</td>
<td>1976±211 (n=4)</td>
</tr>
<tr>
<td>NPS</td>
<td>2758±197 (n=5)</td>
</tr>
</tbody>
</table>

Energy Released per Insertion Comparison

Confirmation of a puncturing event was determined via comparison of the energy released during each insertion (Table 1). For all tissue types, the energy released between the first and second insertions was significantly higher (p<0.05), allowing for confirmation that a puncture had been made during the first insertion. The same results were observed when comparing the energy released between the first and third insertions. This allowed us to conclude that a puncture was made during the first insertion of the needle into the tissue.

Average Penetration Force Comparison

The average penetration force for the IPS (123±17 mN, n=6) was significantly lower (p<0.05) than the average penetration force for the IN (1047±97 mN, n=5) and the NPS (1440±161 mN, n=5). There was no significant difference (p=0.3) between the penetration force for the IN and NPS (Fig. 4). A lack of difference between the IN and NPS penetration force suggests that the needle may be inserting into the underlying nerves when penetrating an intact nerve specimen.

Discussion

Safe and accurate performance of sciatic nerve blocks requires delivery of the anesthetic into the paraneural sheath. Knowledge of the force required to penetrate this connective tissue lining could help guide anesthetic needle insertion into the correct area for optimization of sciatic nerve blocks.

It is only in recent years that the paraneural sheath has emerged as a site of interest for sciatic nerve blocks. Currently, relevant work quantifying the force required to puncture the sciatic nerve has not been performed. However, studies of the mechanics of needle insertion into soft biological tissue do exist; these studies allowed us to compare and validate our force-displacement data. In particular, Mahvash and Dupont’s research has proven to be a useful tool to verify that the force-displacement curves for our tissues are indeed indicative of a successful puncture. Since heart and nerve tissue are both categorized as soft viscoelastic tissues, we were able to qualitatively compare Mahvash and Dupont’s force-displacement curves of needle insertion into a pig heart against our force-displacement curves. Specifically, they note the presence of loading-unloading curves in their graphs, characteristics that are present in our force-displacement graphs, as noted in section 3.2 [7]. Moreover, further literature regarding biological tissue needle insertion has identified the puncture force as the peak force in the force-displacement data, which allowed us to verify our assumption that our peak force was indeed a puncture force [7-8].

Our results showed that the force required to puncture the isolated paraneural sheath is statistically lower than the force required to puncture the isolated nerve and nerve with surrounding paraneural sheath. For this study, we decided to quantify the force required to penetrate the isolated sheath, as it would help us understand how vulnerable the sheath may be to punctures. However, it should be acknowledged that the removal of the sheath from the underlying nerve could be influencing these results. It is possible that separation of the sheath from its native structure compromises the mechanical performance of the sheath by making it more susceptible to punctures at lower applied forces. In this study, the separation of the sheath was performed to represent an idealized scenario where the needle would only penetrate...
the sheath; however, this scenario is not possible in vivo, unless dilation of the space in between the sheath and the epineurium is performed. Additionally, although our tissue was stretched, it was not calibrated to in-vivo conditions. Nevertheless, the results in this study suggest that a smaller force is required to penetrate the paraneural sheath and should be explored further in order to determine if the application of this force on a NPS specimen could lead to puncturing of the tissue.

Clinically, our data suggest that there may be an optimal puncture force that would allow for a reduced risk of nerve puncture when applying local anesthetic within the sheath surrounding the sciatic nerve. The current procedure for performing sciatic nerve blocks involves the use of ultrasound to guide the needle into the desired area; currently, physicians are unable to measure needle-tip force. However, we propose that our results could help anesthesiologists understand the difficulty of targeting the paraneural sheath for anesthetic delivery. Essentially, since there is no clear differentiation between the NPS and IN puncture force, it can be suggested that targeting the nerve as a delivery site may lead to insertion into the nerve and not just the paraneural sheath. Thereby, this study can be used as a guidance for anesthesiologists as a precaution against forceful insertions into the nerve. Another characteristic of sciatic nerve blocks is that needle insertion is tangential to the nerve in order to avoid impacting the underlying nerve; however, this was only supported by qualitative ultrasound images [1-5]. Our results confirm that this is an ideal technique since non-tangential needle insertions, as performed in this study, could impact the underlying nerve due to the lack of difference between the force required to puncture the NPS and the IN. However, to fully support this conclusion, a penetration study in which the insertion is performed tangential to the nerve is required.

**Conclusion**

Quantifying the force required to penetrate the paraneural sheath of the sciatic nerve is key to the optimization of anesthetic delivery for sciatic nerve blocks. Our aim was to determine the forces required to penetrate the paraneural sheath, as well as the underlying tissue in an effort to optimize sciatic nerve block procedures. We were able to successfully puncture the paraneural sheath and we concluded that there is a difference between the force required to penetrate the paraneural sheath and the nerve with overlying paraneural sheath. Future work should focus on understanding whether the force required to penetrate the paraneural sheath is sufficient to penetrate the sheath of an intact sciatic nerve.

**Acknowledgments**

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**References**


Nanostructured Ni@SiO₂ Catalysts for Hydrogen Production via Chemical Looping

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Abstract
To satisfy the ever growing demand for hydrogen for new energy applications as well as synthetic chemistry needs, a more sustainable route of hydrogen production is required. Toward this end, we studied an emerging technology called chemical looping, a periodic reactor operation between the primary reduction reaction and oxidative catalyst regeneration. A nanostructured nickel catalyst was synthesized by a sol-gel process to yield nickel nanoparticles (<10nm) dispersed inside the hollow core of a 35-50nm diameter silica shell. The catalyst was characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) and tested in periodic methane decomposition—catalyst regeneration cycles. Overall, the catalyst displayed exceptional stability for hydrogen production in a chemical looping environment with a promising hydrogen yield for utilization in industrial applications with a minimal carbon footprint.

Keywords: chemical looping; methane decomposition; hydrogen production; core-shell catalysts

Introduction
The steadily rising global population concomitantly increases the demand of bulk industrial chemicals such as ammonia (fertilizer), methanol (plastics, plywood, textiles), as well as of clean energy. Hydrogen (H₂) is an important precursor for a vast range of bulk chemicals production and energy applications (such as fuel cells). It is currently produced from natural gas (mainly methane, CH₄) by any of a variety of gas-phase reactions such as methane steam reforming (CH₄ + H₂O → CO + 3H₂) followed by water gas shift reaction (H₂O + CO → CO₂ + H₂) [1,2,3]. Separation of H₂ from the resulting gaseous mixtures requires expensive and energetically demanding downstream processes. Alternatively, decomposition of methane to produce H₂ and solid carbon (CH₄ → C(solid) + 2H₂) could be a more sustainable process which can address the issue of gas separations while utilizing abundant and inexpensive natural gas [4,5]. Furthermore, this process would allow production of hydrogen streams without generating any CO₂ by-product.

Decomposition of CH₄ requires extremely high temperatures, which are significantly reduced by employing supported metal catalysts (typically metallic nickel, Ni, on metal oxide supports, such as silica, SiO₂) [1]. These catalysts are prone to deactivation due to encapsulation of the active metal species (Ni) by the produced solid carbon or by sintering [1,6]. While extensive efforts focused on prolonging the catalysts’ activity have seen some success, limited work has been reported on regeneration of spent catalysts for continued use [1,6]. The present work applies an emerging technology referred to as “chemical looping” by alternating between H₂ production and catalyst regeneration in a cyclic manner. The process begins in the primary reactor with H₂ production (and thus also carbon deposition on the catalyst). The spent catalyst is then cycled to a second reactor where the carbon is gasified by an oxidizing gas to regenerate the catalyst. The regenerated catalyst then returns to the primary reactor and this “looping” pattern continues (see schematic in Figure 1). Alternatively, the process also can be conducted in a single reactor by alternating the reactor feed periodically between methane and the oxidizing gas.

The primary focus of this work is to evaluate the activity and stability of a novel silica-supported nickel catalyst for H₂ production from CH₄ via chemical looping. Ni is a well-established catalyst for the formation of carbon nanotubes, demonstrating its activity for methane cracking, and SiO₂ is one of the cheapest and most widely used support materials in industrial catalysis. The Ni/SiO₂ system hence formed a logical starting point for the intended studies. It has been widely reported that supported metal catalysts
separate from their support materials due to carbon filament formation, resulting in the lift off of the metal particles from the support [1,6,7]. Regeneration of the catalyst then results in detached metal particles which are either carried out of the reactor with the gas stream or agglomerate and thus deactivate, since large Ni particles have been shown to be far less active for CH4 decomposition than their smaller counterparts [8,9]. We hypothesize that encapsulation of the active Ni particles in the cavity of a porous SiO2 shell could suppress this deactivation mechanism by mechanically confining the particles inside the cavity.

**Methods**

**Catalyst Preparation**

The hollow core-shell catalyst (Ni@SiO2) was synthesized by a reverse microemulsion mediated sol-gel process [10]. Initially, a surfactant (Brij-58) and organic solvent (cyclohexane) were mixed at a 1:4 weight ratio to create reverse micelles—nanoscale spherical structures with polar interiors and nonpolar exteriors. After addition of an aqueous NiCl2 solution and a stabilizer (hydrazine), tetraethylorthosilicate (TEOS) was added as the silica precursor—all of which gathered within the interior of the reverse micelles. Following TEOS hydrolysis, the catalyst precursor was washed and centrifuged in ethanol and dried overnight in a vacuum oven at 25°C. The catalyst was then calcined at 500°C for two hours in air to remove contaminants, such as residual surfactant and salt remnants, and complete the formation of NiO and SiO2. Preparation of the conventional catalyst (Ni-SiO2, as a reference material) with Ni dispersed on the external surface of a SiO2 support followed the same SiO2 preparation as detailed above, but with Ni deposition from the NiCl2 salt precursor via a common and simple incipient wetness impregnation [11]. The chemical identity and structure of the catalysts were then verified using X-ray powder diffraction (XRD)—which showed presence of broad silica reflections, representing the amorphous silica structure, and weak Ni reflections—and transmission electron microscopy (TEM), respectively.

**Stability Testing**

Catalyst stability was evaluated with an SDT Q600 V20.9 Thermogravimetric Analyzer (TGA). After loading the 6mg catalyst sample, it was heated to 800°C in an inert gas stream (N2 – 99.999% pure from Matheson) at 100sccm. The temperature and N2 flowrate was maintained throughout the course of the study. Air (20sccm), CH4 (5sccm), and Ar (20sccm), were used as the oxidizing, fuel, and purge gases (supplied by Matheson – 99.99%, 99.99%, 99.999% pure, respectively). In both stability and reactivity testing, the respective purge gas was used to clear the reactor system of other gases between H2 production and catalyst regeneration half cycles.

**Reactivity Testing**

Reactivity testing was conducted in a fixed bed reactor—a 53cm long, 0.7cm diameter glass tube into which catalyst material is packed into a small section and fixed in place by quartz wool on either end. The
reactor was held isothermally at 900°C by a heating oven around the tube. The oxidizing, fuel, and purge gases were CO₂ (1sccm, 16.7%), CH₄ (1sccm, 16.7%), and He (20sccm), (99.999%, 99.99%, 99.999% pure, respectively). The effluent gas concentration was analyzed by a mass spectrometer. Conversion from relative ion currents produced by the mass spectrometer to gas mole fractions was validated by a carbon balance within +/− 5% error.

Results

Catalyst Characterization

Figure 2 shows the TEM images and schematic representations of the as synthesized catalyst materials. For Ni@SiO₂, 35-50nm SiO₂ is clearly seen to have a central cavity with NiO nanoparticles (d<10nm) inside the cavity. Similarly, Ni-SiO₂ is shown to have roughly the same size SiO₂ spheres (~50nm in diameter) with less than 5nm NiO dispersed on the SiO₂ surface. Additional Ni@SiO₂ TEM images after exposure to reactant gases are shown in the inset of Figure 3, indicating agglomeration of Ni particles limited to within each hollow core. XRD results for these materials (not shown here) show evidence for the presence of NiO (peaks at approximately 2θ = 37.5°, 43°, and 63° [12]). Due to the amorphous nature of the silica support, XRD characterization was unable to identify the SiO₂.

Stability Results

The results of the stability testing across 40 cycles from the TGA using 6mg of catalyst are shown in Figure 3. The yield of carbon (normalized to the amount of Ni catalyst) was calculated based on the differences in weight during the reduction cycles in the TGA. It is important to note the substantial difference between

![Figure 2. TEM images and schematic representations of Ni@SiO₂ (a) and Ni-SiO₂ (b) as synthesized. Inserts show a closer view of the catalysts where smaller (>10nm), darker structures are NiO and the larger (~50nm) structures are SiO₂.](image)

![Figure 3. Variation in carbon yield per cycle for Ni@SiO₂ (dashed line, triangles) and Ni-SiO₂ (solid line, circles) in CH₄ decomposition (5sccm) and air regeneration (20sccm) at 800°C with 6mg of catalyst in the TGA. The inset of the graph shows TEM images of the Ni@SiO₂ as synthesized and after one full cycle—the darker structures are NiO within the larger SiO₂ shells. Note the transition from multiple small catalyst particles before reaction to one larger particle after exposure to the reactant gases at an elevated temperature.](image)
the first and subsequent cycles, but also the consistent stability of the Ni@SiO\textsubscript{2} catalyst over the other 39 cycles in the progression, yielding roughly 0.5 mol C / mol Ni. In comparison, Ni-SiO\textsubscript{2} deactivates rapidly, yielding insignificant amounts of carbon.

Reactivity Results
The TGA is not an appropriate reactor configuration for evaluation of hydrogen production, i.e. evaluation of gas phase reactivity. The sample resides in a small pan located in a spacious gas chamber through which the gases flow, so that gas-solid contact is minimal and not representative of the contacting pattern in a realistic reactor configuration. Hence, reactivity testing was conducted in a more appropriate fixed-bed reactor setup and limited to the Ni@SiO\textsubscript{2} catalyst due to its superior performance in the TGA stability testing.

Figure 4 shows the effluent gas composition during a single reduction half cycle at 800\degree C using 50mg of Ni@SiO\textsubscript{2}. High initial CH\textsubscript{4} conversions (~80%) gradually drop to stable values near 30%. Smaller peaks for CO and CO\textsubscript{2} also are noted. To further evaluate the stability and reactivity of Ni@SiO\textsubscript{2}, another multicycle experiment was conducted at 900\degree C using 20mg of Ni@SiO\textsubscript{2} with CH\textsubscript{4} and CO\textsubscript{2} as the reduction and oxidation gases, respectively. Results are shown in figure 5 and suggest again stable H\textsubscript{2} production after initial deactivation of the catalyst over the first cycle.

Discussion
Stability
The Ni@SiO\textsubscript{2} carriers showed overall excellent stability, but only after an initial significant drop in activity. This initial drop in carbon yield is likely due to the sintering of the small catalyst particles within each hollow silica particle into single, slightly larger particles as evidenced by the inset of Figure 3. Since the CH\textsubscript{4} decomposition occurs at active sites on the Ni surface, agglomeration of many smaller Ni particles into a larger one decreases the amount of surface available for the decomposition, limiting the reaction progress. However, due to the structure of the catalyst, after agglomeration of the Ni nanoparticles in each silica cavity, further sintering of the Ni particles was not possible and steady carbon deposition (and hydrogen production) were maintained over the subsequent

![Figure 4](image-url)

**Figure 4.** Concentration profile of the effluent of the fixed bed reactor with 50mg catalyst under 1:6 CH\textsubscript{4}:Ar, 800\degree C, and atmospheric pressure

![Figure 5](image-url)

**Figure 5.** Molar yields of product gases during the reduction half cycles of the fixed bed multicycle experiment with 20mg catalyst under 1:6 CH\textsubscript{4}:Ar, 900\degree C, and atmospheric pressure
cycles. In the conventional Ni-SiO₂ catalyst, it is likely that substantial sintering occurred already during the first cycle and thus limited the carbon yield in even that cycle. Sintering of the initially small active Ni particles (<10nm) into larger catalyst particles during exposure to high temperatures resulted in large, inactive catalyst particles as previously reported [8,9].

Reactivity
While the reaction showed the expected strong production of hydrogen, formation of CO and CO₂ also was observed to a limited degree. These peaks for CO₂ and CO in the early stage of the reaction are typically the result of the reaction of CH₄ via reaction with the oxidized form of the catalyst via (CH₄ + 4NiO → CO₂ + 2H₂O + 4Ni) and (CH₄ + NiO → CO + 2H₂ + Ni) [13]. Once the NiO particles are reduced to metallic Ni, the remaining metallic particles can only catalyze the non-oxidative decomposition of CH₄ to hydrogen and solid carbon, in agreement with our experimental observations at 800°C (see Figure 4).

Increasing the reaction temperature to 900°C, the catalyst was seen to decrease in activity much more rapidly, as expected and reported previously [1,9]. As a result, since the half cycles were stopped when CH₄ conversions decayed to approximately 25%, the amount of time for each half cycle was very short—typically less than four minutes. This short cycle time and the inexact ending time likely contributed to the slight variability in H₂ yield per cycle (Figure 5). Despite these shortcomings, however, the H₂ production appears to be quite stable in this multicycle experiment with little deviation across cycles 3-10. It is sensible that some shift will occur after the first cycle of operation during the initial exposure of the active catalyst particles to the reactant gases at reaction temperature, similar to the reasoning in Section 4.1.

However, the continual production of CO compounds during the multicycle experiments at this temperature is surprising, and we currently lack a clear explanation for this observation. It is unclear how CO₂ and CO would continue to be produced in each cycle, since the Ni catalyst is reduced to its metallic state and there were not any other sources of oxygen present in the reactor. The regeneration of the carrier occurred with CO₂ as oxidant, and Ni cannot be oxidized by CO₂ at these experimental conditions [14]. One possible explanation could be that during the regeneration of the carriers with CO₂, some amount of CO₂ may sorb sufficiently strongly in the porous and hollow Ni@SiO₂ structure that it is only be released upon reaction with CH₄ during the following half cycle (CH₄ + CO₂ + Ni → 2CO + 2H₂ + Ni) or as the CH₄ simply disrupts its adsorbing interactions with the material as it adsorbs onto the carrier [15,16]. Alternatively, there is also is potential that during each of the 10 cycles, CH₄ does not fully reduce all of the carrier material and subsequent COx profiles following the first would result from reduction of NiO to Ni. However, it is unlikely that a sufficient amount of carrier would remain in the oxidized form (NiO) after 10 cycles; this would also be difficult to detect with XRD at the small size and low weight loading of Ni. Further investigation of this observation is ongoing.

Conclusions
Through the synthesis of a uniquely nanostructured catalyst in which active Ni particles are confined within the hollow core of a porous SiO₂ support, a stable catalyst was designed for the decomposition of CH₄ to produce H₂ and solid carbon. In a chemical looping environment, the unique structure of the catalyst proved to be quite effective in maintaining robust catalytic activity over 40 cycles in the TGA. Additionally, the catalytic activity of this catalyst, even at a relatively low weight-loading of Ni (~8wt. % Ni), is highly promising for hydrogen production. Despite the high H₂ production rate, however, additional investigations into the unexpected formation of COx at high reaction temperature are necessary in order to develop a better understanding for the underlying chemistry and to further optimize the process. Nevertheless, these initial results demonstrate that Ni@SiO₂ has a high potential for simultaneous production H₂ and CO via chemical looping.

Acknowledgments
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Avoiding Bad Bit Patterns for Unreliable DRAM Memory Cells

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Abstract

DRAM memory errors have increased in number due to the scaling of the cells to increase memory density. This issue causes errors that Error Correction Code (ECC) cannot always correct. To increase the time that DRAM will remain functional, this paper introduces several methods to correct errors.

Persistent errors in DRAM seemed to be caused by certain bit patterns surrounding corrupted cells. For the purposes of this study these patterns are chosen to be “111” and “000”. The reason for this choice is explained in more detail in the paper.

Three main techniques were used to correct these. The first was compressing the bits and stuffing inverse bits. This worked only if the data was compressible. The next method was flipping every other bit and the final method was flipping every third bit. These proved to be successful in most cases other than when they would create new bad bit patterns.

After describing these methods and results, this paper provides some conclusions about the findings and insights into future work.

Introduction

As technological demands increase, DRAM (Dynamic random-access memory) has been scaled to a much smaller size to increase memory density. Though this is required to keep up with the demands of technology, it is causing errors. While error correction code (ECC) can correct some of these errors, it is being discovered that some of them are more persistent and, therefore, cannot be handled by ECC. These errors also can cause issues in other nearby cells.

An error is when one singular cell in a row of DRAM generates read or write errors consistently. Corrupted cells are one bit in the row of DRAM that no longer reads or writes the proper value. The errors specifically being discussed in this paper are errors that occur every time a row is accessed and occur in the same cell. [3]

As DRAM has been scaled over the past few years, the rate of soft errors or non-persistent errors has dropped significantly because the smaller size leads to less charge build-up when applying voltage to read or write. Unfortunately, hard errors or persistent errors have not seen a similar decrease in frequency and account for approximately 2% of errors. The density of modern DRAM is creating more issues with persistent errors. Corrupted cells in a row have actually been shown to increase the likelihood that cells in close proximity also will become corrupted. These errors also cannot be easily fixed because they will occur every time charge is passed through the row to read or write. [4]

In this study, three error rates are taken into account, 2%, 5%, and 10%. The first is the most accurate percentage of bad cells that would be found in DRAM. The second two were looked at to see if the created methods could work as the DRAM cells became more corrupted as the technology was used. Toward the end of a DRAM’s lifetime, these higher error rates might be accurate but 2% error would be the most accurate error rate for DRAM in regular use.

The current method for dealing with these bad cells is to replace them with an extra block of good cells. Unfortunately, as the technology is continuing to be scaled, the number of errors is becoming greater than the number of good blocks. If this happens, the entire block has to be marked as bad and cannot be used. This
method was inefficient to begin with because it requires some cells to be unused in the case of a corrupted cell, which is a waste of space in the already dense DRAM. In a market where technology is becoming smaller, there is no room for wasted space like what is used in the current method for dealing with corrupted cells.

Studies into what is causing these issues show that certain bit patterns surrounding a cell make it more likely to misread. These “bad patterns” that need to be avoided are dependent on the circuit layout of memory. For this study, previous research was used to choose the patterns “000” and “111” as the bad patterns.

The reason for choosing these patterns has to do with the fact that this study focuses on DRAM. In DRAM, every time there is a read or write the cell has to receive a voltage. If there is a string of high values or low values and a corrupted cell in the middle of these values, the error will become persistent because every time the row receives voltage the cell will be overwhelmed by the charge of the cells around it. Having all high voltages (111) or all low voltages (000) surround a corrupted cell will only increase the likelihood of this cell to be unreliable. That is why in DRAM repeated values cause so much of an issue for these already corrupted memory cells. This build up or lack of charge will create an issue that ECC cannot fix. [2]

The goal of this research is to fix these bad patterns to ensure that cells will not return false data. Early intervention with architectural solutions will increase the chances that these memory chips will remain reliable.

Methods
In order to solve the issue of data corruption, unusable cells, and bad bit patterns, three basic schemes were created and tested using Pin Tools.

The first scheme used compression to attempt to fix bad cells. If a line contained a bad cell, it would be compressed if possible. After it was compressed, a bit was inserted in between every other cell to break up bad patterns. The bit inserted was always the inverse of the previous bit so it was impossible to have the pattern “000” or “111.” So in this case, the problem would always be solved as long as the line could be compressed.

Lines could be compressed if there were certain patterns found within the line pre compression such as all zeros or a repeating value. A prewritten compression tool was used and edited for this project [1].

The next scheme involved flipping every other bit to break up patterns around bad cells. In this case, when there was a bad cell in a row, the tool would go in and flip every other bit in order to attempt to break up the bad patterns around the corrupted cell.

The final scheme was flipping every third bit. For this portion of testing, the tool would go into the line and flip every third bit starting with the first one. If that left a bad pattern behind, it would try flipping the second bit and if that still left bad patterns, the third was flipped. If all of these choices failed, the line was marked as bad and could not be used in the future.

To read data after the bad cells had been eradicated, there were marker cells placed at the end of a row indicating how the row had been changed to reduce error.

The three schemes were run at the same time and on parsec benchmarks. Each was run for an hour so that the tool had time to get to the main part of the benchmark without having to run each of the tests until they were completed. The tool was run on a total of 11 different benchmarks.

The benchmarks were prewritten and simply downloaded and used for testing purposes in this research. None of them were original material.

Each of these schemes and benchmarks were run three separate times to account for a different error rate seen in DRAM. The error rates tested in this study were 2%, 5%, and 10%. To account for the different error rates, a variable was used in the code when randomly generating the bad cells. The value was set to 0.02, 0.05, and 0.1, respectively, to make that percentage of the total cells corrupted in simulation.

For the results discussed in this paper, the cells that were marked bad were chosen at random and corrected. This is an ongoing study and results will soon be available that mark bad cells based on research into the actual distribution of bad cells in DRAM.
Results
As seen in Figures 1, 2 and 3, the different tools worked extremely well for fixing errors found in DRAM.

The scale on the side is used to indicate the percent of errors fixed by this method. Flipping every third bit almost always fixed errors that it was presented with and corrected about 99% percent of the bad cells. Flipping every other bit was also a viable option as it fixed about 94% of errors. Compression wasn’t the most effective option because, as seen in Figure 1, data is often uncompressible. Because data isn’t always compressible, that method will fail frequently and unpredictably.

As the percentage of bad cells in DRAM increased, the effectiveness of every type of correction decreased significantly.

Discussion
So far, the best option seems to be flipping every third bit. That method almost always eradicated the bad patterns and would be the best option for salvaging the greatest amount of usable space in DRAM. The other two methods did not fail horribly, however. They were each able to save some space in DRAM and could also be considered viable options.

As the amount of bad cells in DRAM increased, the different correction methods became much less efficient. This is because if there are multiple cells in a row, flipping every other or every third bit might fix one of the bad patterns, but might create another one. So if flipping every third bit fixes 111 around one cell, it might create a pattern of 000 or 111 around another corrupted cell. This only occurs when there are a large amount of bad cells in one row and very close to each other. Unfortunately in real DRAM this is often how the corrupted cells are spaced out due to the fact that an error in one cell can induce errors in other adjacent.

Using the third bit flip method would really help to insure DRAM remains reliable with use. The current method for dealing with these cells would be to just mark them as bad and not use them in the future. The method of simply flipping every third bit would save 99% of these cells and ensure that the user still had room for their data in DRAM. Flipping bits doesn’t take up any extra space in memory and requires little tampering with the data to ensure that it is readable for the user. A simple change like this could save a huge amount of space.
This study is really just the beginning of the discussion of how to fix these bad patterns and attempt to save cells in DRAM before just marking them as unusable. This first test of ideas shows that independently, each method works pretty well. But a combination of methods could fix these errors 100% of the time.

If used together, compression and flipping bits could save almost all of the cells that would otherwise be marked as unusable. First, an attempted compression could be used. If that doesn’t work, the tool could simply go back and flip every third bit. And on the very small chance that neither method worked, every other bit could be flipped. This study is just the beginning of how to think about fixing these cells.

As technology becomes smaller and these errors become more prevalent, something will have to be done to ensure that some of the space remains usable. Advancements will be less meaningful if the data that people need becomes unreliable, so this problem needs to be dealt with quickly.

**Conclusions**

The current methods of dealing with persistent corruption in DRAM cells can definitely be improved upon. These results of this study show that much simpler and more space efficient methods can be used to produce results similar to what is currently seen. These results are an improvement over the current methods because they will continue to work for the lifetime of the DRAM. In the current method, if the cells to correct bad data are all used and another error occurs it has to mark and entire row as bad which would never occur in the method proposed in this paper.

A combination of the methods proposed in this paper would be extremely efficient and could potentially solve every error it was presented with. That idea could be used in future studies regarding persistent error correction in DRAM cells. These results should be used as a starting point in the discussion of how to completely eradicate bad cells from DRAM. Hopefully with further research into this topic, DRAM life span will be greatly increased and these techniques can be applied to other forms of memory.

**Acknowledgments**

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Influence of Powder Atomization Techniques and Sintering Temperature on Properties of 3D Printed Alloy 625 Parts
Eamonn Hughes, Amir Mostafaei, and Dr. Markus Chmielus
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Abstract
Powder-bed binder-jet 3D printing has great potential to play a significant role in the manufacture of finalized parts, but the specifics of how well certain metals and alloys can be manufactured by this method are not fully understood. This study uses three types of alloy 625 powders: air-melted water atomized (WA), vacuum-melted argon atomized (AA), and air-melted nitrogen atomized (NA). Samples were printed using an ExOne M-Flex printer and sintered under vacuum at 1220 °C, 1240 °C, 1250 °C, 1260 °C, 1270 °C and 1280 °C for four hours. Before sintering, WA samples were significantly less dense than AA or NA samples (43% vs. 53% and 55%, respectively) due to a lower packing density of the irregularly shaped WA powder particles. After sintering, WA samples did not achieve near full density at any sintering temperature while AA and NA both did so at 1260 °C and above. Mechanical properties reflect this in that AA and NA samples consistently showed higher hardness, tensile strength, and elongation than WA samples under optimum conditions. At above-optimum temperatures, grain growth becomes more pronounced, which negatively affects mechanical properties.

Keywords: Additive manufacturing; Alloy 625; Sintering; Microstructure observations; Densification.

Introduction
Additive manufacturing (AM) or 3D printing has the potential to revolutionize the manufacturing process and is expanding from more limited rapid prototyping applications to production of finalized parts especially those with complex shapes that are not possible to produce through traditional manufacturing methods. Yet, the influence that AM methods have on microstructure and properties of parts is not yet well understood.

One AM method that is able to build metal parts is powder bed binder jet printing in which a machine repeatedly lays down a thin layer of powder and deposits binder according to a CAD model for as many layers as necessary to complete the part [1]. The part is then cured in an oven after which it can be handled, though it is still quite fragile. The part must then be sintered at a high temperature to densify it. This stage is of particular interest because the sintering conditions such as holding time, holding temperature, and sintering atmosphere all have profound effects on the final properties of the part. The methods used to atomize a metal into fine particles also affect the properties of the part since the powders have different shapes, sizes, and impurities.

Zhao et al. studied the porosity behavior in gas and water atomized samples of stainless steel 420 and found that gas atomized powders (GA) were spherical in shape while WA powders were irregularly shaped [2]. This is due to the rapid cooling and solidification caused by the water atomization process preventing the formation of thermodynamically favorable spherical shapes. He observed that GA powders have a high packing density relative to water atomized (WA) powders; however, WA powder based parts tended to sinter at lower temperatures in a shorter amount of time and generally to a higher final density and lower total porosity [2].

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The nickel-based alloy 625 (also referred to as Inconel 625), one of the most successfully applied superalloys in engineering applications [3], is most widely used in aeronautics, chemistry, and marine applications, due to its good corrosion resistance and high stress and strain resistance.

The goal of this study is to determine the influence of powder type and sintering temperature on the properties of AM alloy 625 samples.
**Methods**

In this work, three different alloy 625 powders were used. Scanning electron microscopy (SEM) micrographs are shown in Figure 1: air-melted water atomized (WA), vacuum-melted argon atomized (AA), and air-melted nitrogen atomized (NA). The composition of the various alloy 625 powders is given in Table 1.

Cylindrical coupons with the dimensions of 15 mm diameter and 7.5 mm height along with standard-sized dog bone samples were printed on the ExOne M-Flex 3D printer and then cured at 175 °C for 8 h in a JPW Design & Manufacturing furnace (model ST333ATUL480V9KWC). Samples were then sintered in an alumina powder bed inside a Lindberg/Blue STF54434C tube furnace under vacuum using a Pfeiffer MVP 020-3 AC vacuum pump with different holding temperatures (1220 °C, 1240 °C, 1250 °C, 1260 °C, 1270 °C, and 1280 °C) for 4 h. The general sintering profile, based in part on manufacturer recommendations, is to heat at 5 °C/min to 600 °C, 3.2 °C/min to 1000 °C, 2.8 °C/min to the holding temperature (between 1220 and 1280 °C), hold for 4 h, and then cool at 1 °C/min to 1200 °C, 3.1 °C/min to 500 °C and finally to room temperature. Figure 2 provides an illustration of the temperature profile for the sintering process.

The density of the sintered samples were measured with an Ohaus AX324 precision balance using Archimedes’ water immersion method both taking into account the temperature of the water and the buoyancy of the air. The unsintered samples were measured simply by weight and volume since they could not be submerged in water. Sintered samples were ground, polished, and then imaged using a Keyence digital optical microscope. The micrographs were analyzed using ImageJ to determine the area density.

The samples were tested for hardness using Vickers microhardness test method with a Leco LM 800 under a load of 100 gf and with a dwell time of 10 s. Five tests were done for each sample and the hardness value ranges were calculated.

The dog bone samples were sintered under the optimal conditions for the powder type and tested for tensile strength using a Mechanical Test System (MTS 880) with tests conducted at a deformation rate of 5 mm/min.

**Table 1.** Chemical composition and powder size of the alloy 625 powders provided by the manufacturers

<table>
<thead>
<tr>
<th>Elements</th>
<th>Composition in atomic weight percent (wt %)</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Water atomized</td>
<td>Bal.</td>
<td>21.80</td>
</tr>
<tr>
<td>Vacuum-Ar atomized</td>
<td>Bal.</td>
<td>21.4</td>
</tr>
<tr>
<td>Air-N atomized</td>
<td>Bal.</td>
<td>21.5</td>
</tr>
</tbody>
</table>
Results
Values for the percent densification, 

\[
\frac{\text{density of sample}}{\text{density of material}} \cdot 100 = 1 - \text{porosity},
\]

of the printed, unsintered samples are summarized in Table 2.

Table 2. Percent densification of unsintered samples

<table>
<thead>
<tr>
<th>Percent Densification - Printed, Unsintered Samples</th>
<th>Water</th>
<th>Argon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>42%</td>
<td>53%</td>
<td>55%</td>
</tr>
</tbody>
</table>

The results of the sintered sample densification measurements are summarized in Figure 3 and Figure 4. In general, WA samples have lower porosity at lower sintering temperatures and higher porosity at higher sintering temperatures than NA and AA samples. Additionally, the porosity tends to decrease with increasing sintering temperature particularly for AA and NA samples but less so for WA samples. It should be noted that at higher temperatures, samples began to show evidence of melting. This was apparent from a distinct rounding of the initially sharp edges of the cylindrical samples. More severe melting resulted in samples rounding into a half sphere shape. This occurred at and above 1250 °C for WA, 1260 °C for AA, and 1280 °C for NA.

Figure 5, Figure 6, and Figure 7 show optical microscopy micrographs of a selection of sintering temperatures for samples of each powder type.

![Figure 3](image3.png)

Figure 3. Percent densification of sintered samples measured by water immersion method

![Figure 4](image4.png)

Figure 4. Percent densification of sintered samples measured by optical microscopy

![Figure 5](image5.png)

Figure 5. Optical microscopy (OM) micrographs of WA samples at (top to bottom) 1220 °C, 1240 °C, 1260 °C, and 1280 °C at x100 (left) and x1000 (right)
Figure 8 shows scanning electron microscopy (SEM) micrographs of each sample type showing pores and grain boundaries. Particularly noticeable for WA and NA samples are the lighter areas at the grain boundaries along with the pores generally along the grain boundaries.

Table 3 shows the hardness values for each sample type at each sintering temperature. Each sample type exhibits increasing hardness values with increasing temperature until it reaches a peak after which it decreases. The approximate peak hardness temperatures are at 1250 °C for WA, 1260 °C for AA, and 1270 °C for NA.

Figure 7. OM micrographs of NA samples at (top to bottom) 1220 °C, 1240 °C, 1260 °C, and 1280 °C at x100 (left) and x1000 (right)

Figure 6. OM micrographs of AA samples at (top to bottom) 1220 °C, 1240 °C, 1260 °C, and 1280 °C at x100 (left) and x1000 (right)

Table 3. Microhardness values for each sample type at each sintering temperature

<table>
<thead>
<tr>
<th>Microhardness Values (HV$_{0.1}$), 5 measurements each</th>
<th>Water Atomized</th>
<th>Argon Atomized</th>
<th>Nitrogen Atomized</th>
</tr>
</thead>
<tbody>
<tr>
<td>1220 °C</td>
<td>149 ± 12</td>
<td>107 ± 25</td>
<td>160 ± 15</td>
</tr>
<tr>
<td>1240 °C</td>
<td>163 ± 11</td>
<td>215 ± 18</td>
<td>184 ± 13</td>
</tr>
<tr>
<td>1250 °C</td>
<td>192 ± 7</td>
<td>227 ± 9</td>
<td>192 ± 7</td>
</tr>
<tr>
<td>1260 °C</td>
<td>183 ± 7</td>
<td>237 ± 5</td>
<td>197 ± 8</td>
</tr>
<tr>
<td>1270 °C</td>
<td>174 ± 9</td>
<td>197 ± 5</td>
<td>202 ± 6</td>
</tr>
<tr>
<td>1280 °C</td>
<td>170 ± 5</td>
<td>185 ± 4</td>
<td>201 ± 6</td>
</tr>
</tbody>
</table>

Figure 8 shows scanning electron microscopy (SEM) micrographs of each sample type showing pores and grain boundaries. Particularly noticeable for WA and NA samples are the lighter areas at the grain boundaries along with the pores generally along the grain boundaries.

Table 3 shows the hardness values for each sample type at the various sintering temperatures. Each sample type exhibits increasing hardness values with increasing temperature until it reaches a peak after which it decreases. The approximate peak hardness temperatures are at 1250 °C for WA, 1260 °C for AA, and 1270 °C for NA.
The results of the tensile tests are summarized in Figure 9 and Table 4. Each sample tested was sintered at the optimum temperature as determined by porosity and hardness results. The results show that WA samples performed the poorest for measures of elastic modulus, elongation, and tensile strength. NA performed significantly better, and AA performed the best by these measures.

### Discussion

#### Densification

As shown in the results, the unsintered WA samples have the lowest density by a significant margin due to the lower packing ability of its irregularly shaped powder particles. The densification results for the sintered samples indicate that the sample densification generally increases with increasing sintering temperature. At a certain point, samples begin to show evidence of melting which is undesirable in sintering; therefore, sintering temperatures must be kept below this level. Temperatures near the melting point (1290 °C–1350 °C for alloy 625 [5]) of the material and long holding times cause grain coarsening that lowers strength and causes elemental segregation at the grain boundaries, which decreases toughness [4]. Evidence of this is shown in Figure 8 where the lighter colored areas are believed to be lower melting point elements of the alloy that separated from the grains into the grain boundaries.

The porosity results at the sintering temperature of 1220 °C for alloy 625 agree with Zhao’s results on stainless steel 420 [2] that WA powders sinter faster and at lower temperatures than GA samples; however, the results of this study do not agree with Zhao’s result that WA samples achieve higher densities.

Additionally, it is noteworthy that the porosity does not decrease for WA samples beyond 5%, yet AA and NA samples decrease porosity to <1%. This is supported by Figure 5, Figure 6, and Figure 7, which clearly show a relatively consistent level of porosity for WA and a dramatic decrease in porosity for both AA and NA. This is likely due to the higher initial porosity of the unsintered WA samples preventing full densification because of the large number of pores that need to migrate out and the large volume shrinkage required of the sample.

The variation between water immersion and optical microscopy density measurements, particularly the drop in density at 1270 °C for water immersion measurements, is most likely due to alumina particles that stick to the sample when it slightly melts during sintering. While water immersion averages the density of the entire sample (including low density alumina at the surface), optical microscopy micrographs were only taken in the center of the samples.

#### Microstructure Properties

The properties of WA samples will be dominated by the high porosity making a thorough examination of the microstructure less insightful. Only the AA and NA microstructures, therefore, require more in-depth examination. Increasing the sintering temperature indeed increases the grain size as shown in Figure 6 and Figure 7, though difficult to see. This grain growth is why it is important to not sinter at too high a temperature.
Furthermore, one can observe that the pores in both AA and NA are located along the grain boundaries for the most part. This will prove detrimental to the strength of both samples since these pores’ locations will lower the resistance to slipping of the grain boundaries.

**Mechanical Properties**

The mechanical properties of the samples broadly reflect what one would expect based on the densification data. In general, fully densified samples exhibited higher hardness, higher tensile strength, and better elongation. At low sintering temperatures, samples have low hardness due to their highly porous nature. This is supported by the sharp jump in the hardness of AA from 1220 °C to 1240 °C which is accompanied by a sharp increase in density. NA also shows a jump across this range but not as great as that of AA due to the smaller increase in density. Overall it seems that at the lower temperatures, the hardness of a sample is strongly correlated with its level of porosity. Samples then reach a peak hardness, which generally corresponds with reaching near full density. After this point, higher temperatures and longer hold times only promote growth of grains, which decreases the strength and hardness of the samples [3-5].

Tensile tests for the optimal sintering conditions for each powder indicate that AA powder achieves the best properties in terms of tensile strength and elongation. The WA sample exhibits behavior more characteristic of a brittle material due to its significant residual porosity. While the AA and NA samples both show ductile behavior characteristics, AA performs better with higher yield strength, tensile strength, and elongation.

**Conclusions**

Alloy 625 samples printed with water atomized powder sinter faster and at lower temperatures than those printed with gas-atomized powder, but not to full density. Nitrogen and argon atomized powder samples sinter to near full density and as a result demonstrate much better mechanical properties such as hardness, tensile strength, and elongation than water atomized samples. Mechanical properties may be further increased through an aging process, which has been demonstrated to cause phase precipitation, which increases strength and hardness. The potential for this should be investigated in the future.

**References**


**Acknowledgments**

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Implementation of Butterworth Filtering to Improve Beat Selection for Hemodynamic Analysis of Heart Failure Patients Referred for Left Ventricular Assist Device

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Abstract
Generation of an average representation of pressure signals from multiple cardiac cycles is a common hemodynamic analysis technique. When a pressure waveform is not properly divided into individual cardiac cycles, the clinical relevance of analysis results is diminished. This study’s aim was to include more cardiac cycles in the generation of an average representative beat (ARB) while limiting the usage of single beats for analysis by implementing a Butterworth (BW) filtering-based system.

Pre-operative right ventricular pressure waveforms from right heart catheterizations of 25 patients prior to left or biventricular assist device implantation were obtained. Two methods were used for post-processing: 1) Savitzky-Golay (SG) filtering-based system divided cycles at end diastolic pressure (EDP) by finding diastolic blood pressure (DBP) and adding 6 mmHg to simulate EDP; 2) BW filtering-based system used the 2nd derivative of pressure to calculate EDP, and divided cycles between DBP and EDP. The resulting ARB from selected cycles was analyzed. Results were compared via Bland-Altman analysis. Ability to generate ARB and analyze more patients was evaluated by standard statistical methods.

Bland-Altman analysis determined clinical equivalence of outputs (except EDP) from BW and SG filtering-based methods. EDP disparities were attributed to the differences in methods of calculations. In addition, the BW filtering-based method was found to significantly increase beat alignment for generation of ARB while allowing analysis of more patients. By increasing the reliability and repeatability of outputs, we strengthen the potential diagnoses that result from our analysis.

Keywords: Hemodynamics; Butterworth filtering; Right heart catheterization; Right ventricular pressure

Introduction
Due to the shortage of donor hearts available for transplant, mechanical circulatory support is the best therapeutic option for many patients with end stage heart failure. However, 15–25% of patients who receive left ventricular assist device (LVAD) implants end up developing right ventricular (RV) failure [1]. It is important to identify patients at risk of RV failure prior to LVAD implant because these patients have better outcomes when initially given biventricular support [2]. A common clinical diagnostic technique to assess RV function is analysis of pressure waveforms obtained via right heart catheterization (RHC), a procedure in which pressure generated within the RV is directly recorded. Commonly use parameters include diastolic blood pressure (DBP; minimum pressure), systolic blood pressure (SBP; maximum pressure), end diastolic pressure (EDP; pressure immediately before contraction), dP/dt\textsubscript{max} (rate of contraction), and dP/dt\textsubscript{min} (rate of relaxation).

During hemodynamic analysis of RV pressure waveforms, we commonly generate an average representative beat (ARB) from multiple cardiac cycles. Inability to align cardiac cycles due to improper cycle division and artificial phase shifts can generate inconsistent results, limiting their significance. This misalignment either leads to: 1) use of a single beat which may not be representative of the entire pressure waveform for analysis; or 2) exclusion of the patient sample from further analysis.
The importance of proper filtering and cycle division is paramount when dealing with VAD patients because they are small in number and often have erratic RVP waveforms containing high frequency noise. The lab’s current method of filtering and cycle division employed a Savitzky-Golay (SG) filter. SG filters smoothen data by applying a least-squares fit of an \( n \)th order polynomial in the time domain to window of data, but are plagued by limitations in stopband attenuation [3]. We hypothesized that a Butterworth (BW) filter would improve the ability to perform multiple beat selection, improving consistency and repeatability, without significantly altering data outputs from the analysis program. A BW filter was chosen because it is simple to implement, has a maximally flat pass-band, and good attenuation in the stopband [4,5]. The BW filtering method was compared to the SG filtering method indirectly by examining ARB generation, and directly by Bland-Altman analysis of measured parameters.

Methods
Right Heart Catheterization Procedure
This project was approved by the University of Pittsburgh Institutional Review Board. Swan-Ganz fluid filled catheters (Edwards Lifesciences, Irvine, CA), sampled at 1 kHz, were used to perform a standard RHC. The Witt Biomedical Catheter System (Phillips Healthcare, Andover, MA) was used to collect hemodynamic data and capture images of the waveforms.

Patient Cohort
This protocol was applied to 31 patients from UPMC Presbyterian Hospital who were referred for LVAD or biventricular assist device (BiVAD) implantation. The pre-operative data was retrospectively obtained (after LVAD implantation) in 26 patients and prospectively obtained (at time of RHC procedure, prior to LVAD implantation) in five patients. One patient was excluded from analysis due to inability to analyze RVP waveform.

Retrospective Data Acquisition
Retrospective data acquisition involved redigitizing electronic image files as the data was not stored in digital format, a method we have previously reported [6]. Briefly, Joint Photographic Experts Group (JPEG) image files were obtained from the WITT system and uploaded into a custom MATLAB script. Redigitization was performed by selecting waypoints along the RVP waveform and constructing a line via cubic piecewise polynomial interpolation. The values of each point along the line were generated by user assignment of pressure and time scales and a point of origin. The script exported these values as a text file which was used for further analysis.

Prospective Data Acquisition
At the time of pre-operative RHC, the binary out function of the WITT system was used to obtain a text file containing the time and pressure data (\( n=5 \)). The data was imported into a custom MATLAB program for analysis.

Savitz-y-Golay Filtering-Based Method
The previous method employed a SG filter to smoothen the data. The filter locally fit the pressure waveforms to 3rd order polynomials over a frame size of 11 data points. Cardiac cycles were identified by finding maximum pressure points (SBP), and dividing beats from peak to peak. To include an entire heartbeat in each cycle, the minimum pressure (\( P_{\text{min}} \)) was found in each peak to peak interval. The pressure waveform was scanned for the last point that was 6 mmHg greater than \( P_{\text{min}} \), simulating EDP, and the cycles were divided there (Figure 1).

Butterworth Filtering-Based Method
The new method passed the pressure signal through a 3rd order low-pass BW filter that used a corner frequency (\( \omega_c \)) of 30 Hz, which adequately removed high frequency noise while preserving beat magnitude and morphology. A 3rd order filter was chosen because

![Figure 1. Savitz-Golay Cycle Division Method](image-url)
RHC pressure waveform is shown in the black line. Vertical blue lines represent \( P_{\text{min}} \); vertical red dotted lines represent where EDP is simulated; distance between \( P_{\text{min}} \) and EDP is inconsistent.
it provided sufficient attenuation while limiting computational complexity. The method then identified cardiac cycles using SBP and divided the beats into peak to peak intervals. It found the first minimum (DBP) that occurred below a threshold (mean of the pressure waveform). This method identified the location of EDP using the 2nd derivative of pressure filtered at $\omega_c = 10$ Hz – additional filtering made location identification easier where magnitude preservation was unimportant. EDP was identified to occur at the maximum of the 2nd derivative that preceded the location of the cycle maximum of the 1st derivative of pressure ($dP/dt_{\text{max}}$). The cardiac cycles were then divided at 1/3 of the way between DBP and EDP. Figure 2 illustrates how EDP is calculated and how the cycles are divided using DBP and EDP.

Average Representative Beat Selection and Analysis
The individual cycles were superimposed to aid in selecting those with similar phase and morphology (Figure 3). Dissimilar cycles, including ectopic beats and premature ventricular contractions, were deselected and the remaining similar beats were averaged to create an ARB. The ARB was used for calculations of steady state parameters: heart rate (HR), diastolic blood pressure (DBP), SBP, mean arterial pressure (MAP), $dP/dt_{\text{max}}$, $dP/dt_{\text{min}}$, and EDP. Additionally, it was used for calculation of the diastolic time constant (Tau) [7].

![Figure 2. Butterworth Cycle Division Method](image)

From top to bottom, the black lines represent a RVP waveform and its 1st and 2nd derivatives. DBP (red circle) was calculated from the minimum of the pressure signal. $dP/dt_{\text{max}}$ (blue diamond) was calculated from the 1st derivative. EDP (orange square) was determined from the 2nd derivative. Cycles were divided (red lines) 1/3 of the way between DBP and EDP.

![Figure 3. RVP Waveform with Cycle Divisions Using Each Method](image)

Panel A contains the entire RVP waveform of one patient. The cycles that are overlaid in panels B and C are highlighted in red. Panel B contains the overlaid cardiac cycles after applying the Savitzky-Golay method. Panel C contains the cardiac cycles from division using the Butterworth method. In both panels B and C, the cycles used for average representative beat generation are in solid, bold lines. The deselected cycles are shown by the dotted lines.
Statistical Analysis
Results from each patient were compiled using a custom MATLAB script that generated Bland-Altman analysis plots. Bland-Altman analysis is a standard approach for comparing two different methods of measuring a clinical parameter by plotting the mean measurement of the two methods against the difference of the methods [8]. The bias is calculated as the mean of the differences and limits of agreement are the bias plus/minus two times the standard deviation of the differences. When a parameter exhibits a standard deviation that varies with the mean, the bias and limits of agreement are transformed via regression [9]. Between group comparisons were made using a Student T-test and/or McNemar’s Test (SPSS Statistics version 20, IBM Corp, Armonk, New York).

Results
Generation of the Average Representative Beat
Steady state analysis was performed on each of the 25 patients whose RHC waveforms were retrospectively obtained. Additionally, Tau, a logarithmic model of pressure decay during ventricular relaxation and considered a gold standard measure of ventricular diastolic function, was able to be calculated for 21 patients; four were excluded for unreliable logarithmic curves. The BW method increased the average number of beats used (4.3 ± 2.5 vs 2.2 ± 1.1, P = 0.003) and decreased the number of patients for which only a single beat was used (6 vs 1, P = 0.025).

Bland-Altman Analysis of Steady State Results for the Retrospective Data (n=25)
Table 1 contains the bias and standard deviation from the Bland-Altman analysis of each parameter measured from the ARB. No clinically relevant bias existed between the two methods for all parameters except EDP, dP/dt\(_{max}\) and dP/dt\(_{min}\). Of these, only dP/dt\(_{max}\) exhibited a linear trend of significantly increasing bias with increasing mean value.

<table>
<thead>
<tr>
<th>Steady State (n=25)</th>
<th>Output</th>
<th>HR (bpm)</th>
<th>SBP (mmHg)</th>
<th>DBP (mmHg)</th>
<th>MAP (mmHg)</th>
<th>EDP (mmHg)</th>
<th>dP/dt(_{max})* (mmHg/s)</th>
<th>dP/dt(_{min}) (mmHg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias**</td>
<td>0.73</td>
<td>0.09</td>
<td>0.08</td>
<td>0.18</td>
<td>7.0</td>
<td>0.27x-67</td>
<td>-70.7</td>
<td></td>
</tr>
<tr>
<td>SD***</td>
<td>7.4</td>
<td>2.7</td>
<td>2.1</td>
<td>1.6</td>
<td>6.6</td>
<td>0.04x+18.1</td>
<td>76.4</td>
<td></td>
</tr>
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<table>
<thead>
<tr>
<th>Diastolic/ Tau (n=21)</th>
<th>Output</th>
<th>Tau Half (s)</th>
<th>Tau Exponent (s)</th>
<th>Weiss (s)</th>
<th>Bias**</th>
<th>SD***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias**</td>
<td>-0.003</td>
<td>-0.003</td>
<td>-0.01</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SD***</td>
<td>0.005</td>
<td>0.005</td>
<td>0.06</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* Transformed: Linear regressed bias and SD
**Bias = Mean of Differences; Offset from 0
***Limit of Agreement = Bias ±

Table 1. Bias and Standard Deviation from Bland-Altman Analysis of Retrospective Data
Table 2. Bias and Standard Deviation from Bland-Altman Analysis of Prospective Data

<table>
<thead>
<tr>
<th>Output</th>
<th>HR (bpm)</th>
<th>SBP (mmHg)</th>
<th>DBP (mmHg)</th>
<th>MAP (mmHg)</th>
<th>EDP (mmHg)</th>
<th>dP/dt_{max} (mmHg/s)</th>
<th>dP/dt_{min} (mmHg/s)</th>
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</thead>
<tbody>
<tr>
<td>Bias*</td>
<td>0.13</td>
<td>0.51</td>
<td>1.81</td>
<td>1.5</td>
<td>9.3</td>
<td>-30.3</td>
<td>-55.1</td>
</tr>
<tr>
<td>SD**</td>
<td>2.3</td>
<td>2.5</td>
<td>2.0</td>
<td>2.3</td>
<td>5.0</td>
<td>40.8</td>
<td>148.1</td>
</tr>
</tbody>
</table>

Diastolic/ Tau (n=4)

<table>
<thead>
<tr>
<th>Output</th>
<th>Tau Half (s)</th>
<th>Tau Exponent (s)</th>
<th>Tau Weiss (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias*</td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.08</td>
</tr>
<tr>
<td>SD**</td>
<td>0.04</td>
<td>0.04</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*Bias = Mean of Differences; Offset from 0
**Limit of Agreement = Bias ± 2*SD

Table 3. Bias and Standard Deviation from Bland-Altman Analysis of Redigitized Data

<table>
<thead>
<tr>
<th>Output</th>
<th>HR (bpm)</th>
<th>SBP (mmHg)</th>
<th>DBP (mmHg)</th>
<th>MAP (mmHg)</th>
<th>EDP (mmHg)</th>
<th>dP/dt_{max} (mmHg/s)</th>
<th>dP/dt_{min} (mmHg/s)</th>
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<tbody>
<tr>
<td>Bias*</td>
<td>0.66</td>
<td>1.7</td>
<td>1.8</td>
<td>1.5</td>
<td>7.6</td>
<td>53.6</td>
<td>-62.0</td>
</tr>
<tr>
<td>SD**</td>
<td>4.6</td>
<td>2.4</td>
<td>1.9</td>
<td>1.8</td>
<td>3.6</td>
<td>34.6</td>
<td>56.9</td>
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Diastolic/ Tau (n=4)

<table>
<thead>
<tr>
<th>Output</th>
<th>Tau Half (s)</th>
<th>Tau Exponent (s)</th>
<th>Tau Weiss (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias*</td>
<td>0.002</td>
<td>0.000</td>
<td>0.01</td>
</tr>
<tr>
<td>SD**</td>
<td>0.004</td>
<td>0.001</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Bias = Mean of Differences; Offset from 0
**Limit of Agreement = Bias ± 2*SD

Bland-Altman Analysis of Steady State Results for the Prospective Data (n=5)

Tables 2 and 3 show the Bland-Altman plots of the same parameters, exploring the differences between analysis on prospective and redigitized data for each of the two methods. Results were comparable using prospectively acquired digital data (Table 2) or redigitizing the images of the waveforms as done for the retrospective cohort (Table 3). Similar to the retrospective cohort, the prospective data exhibited minimal bias for all outputs except for EDP, dP/dt_{max}, and dP/dt_{min}, for which the bias persisted. No linear trend for bias was observed for the prospective data.

Discussion

These findings show that the BW filtering-based method of beat division improved ARB generation by allowing the user to select a larger number of beats per patient. Additionally, it reduced the number of cases where a single beat would need to be used to represent the entire capture because of improper cycle division.

The Bland-Altman analysis of the retrospective data (n=25) showed consistency of all outputs except for the values of EDP and dP/dt (max and min). The difference in EDP values was expected because of the different techniques that the two methods used to calculate EDP: The SG method found P_{min} by adding 6 mmHg, as opposed to the BW method using the 2nd derivative of pressure to calculate EDP. For the dP/dt comparisons, a bias of 50 mmHg/s is relatively insignificant, representing only 10% or less of the mean dP/dt values (ranging to above 1000 mmHg/s). However, the relevant entity is the linear trend that exists as the mean values increase (dP/dt_{max}). This trend indicates that as the value of dP/dt_{max} increases, the SG method is underestimating the parameter or the BW method is overestimating the parameter. However, since the data was redigitized from an image, it is impossible to know which method
is correct without a true signal for comparison. Additionally, by transforming the Bland-Altman plots, they can be used to demonstrate equivalence as long as the transformation equation is considered.

By analyzing the small prospectively obtained data set, it was hoped that the optimal method could be determined. However, none of the patient’s that were analyzed had high \( \Delta P/\Delta t_{\text{max}} (>500 \text{ mmHg}) \) values. Therefore, even though the Bland-Altman analysis did not reveal a linear trend in bias, we can not rule out that it would not be present at larger values of \( \Delta P/\Delta t_{\text{max}} \). The prospective data set also provided validation of the redigitization process as compared to a true digitally recorded signal.

**Study Limitations and Future Direction**

Bland-Altman analysis only determines the equivalency of two methods, not which method is superior [8]. As a result, method superiority could only be determined qualitatively via visual inspection, and through limited quantitative analysis of ARB generation. Prospective data was of limited sample size, limiting interpretation. Future work will involve expanding the prospective set and evaluation of method superiority using normalized cross-correlation of each method to a gold standard ARB obtained via manual cycle division. Additionally, the potential clinical implications of the differences in EDP and \( \Delta P/\Delta t \) values will need to be explored.

**Conclusion**

The BW method shows promise as a replacement to the SG filtering method currently in place. It significantly improves generation of an ARB by allowing use of more beats per patient while limiting use of single beats. Additionally, the outputs of the BW method do not significantly differ from those of the SG method for most measures of interest. Accordingly, the outputs are equivalent to the previous method, but reliability and repeatability have been increased with the BW method, which likely will improve clinical diagnostic utility of this hemodynamic analysis.

**Acknowledgments**

Funding provided by the University of Pittsburgh Swanson School of Engineering, the Office of the Provost, and NIH TPPG P01 HL103455. Signal processing advice was given by Dr. Kang Kim, Nadim Farhat, Xuan Ding, and Jaesok Yu of the University of Pittsburgh Multi-Modality Biomedical Ultrasound Imaging Lab.

**References**


Optimal Design of a Pharmaceutical Distribution Network

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*Department of Industrial Engineering, University of Pittsburgh, Pittsburgh, PA, USA

Abstract
This paper discusses the organizational structure of the discrete cost components that will be incorporated in a tool to aid healthcare professionals. The proposed tool will enable a consistent means of optimally designing cost-effective health system pharmaceutical distribution networks. At the macro level, use of a central warehouse that serves multiple hospitals is weighed against a decentralized system of individual hospital pharmacies for pharmaceutical receiving and bulk storage. At the micro level, a centralized cart-fill process is compared to unit-level ADC (automated dispensing cabinet) storage for in-hospital distribution. These macro and micro levels are reduced to their most basic components for inclusion in cost and optimization models. The existing literature was supplemented by data and domain knowledge provided by Geisinger Health System staff. A pharmaceutical distribution cost model, constructed in Excel, serves as a basis for the development of optimization models for warehouse location, transport routing, and pharmaceutical delivery pathway assignment. Future data collection will improve cost driver estimation and guide optimization model enhancements. Ultimately, this study lays the groundwork for the construction of a comprehensive tool that’s goal is to reduce healthcare costs by minimizing distribution expenses.

Keywords: Pharmaceuticals; Distribution; Hospital system; Healthcare

Introduction
With pressure to reduce spending, U.S. hospitals are seeking ways to lower operational costs. Representing a significant portion of hospital expenditures, pharmaceuticals are an ideal area of focus for optimization and cost reduction. Transportation, facility, staffing, equipment, and inventory holding costs are influenced by distribution system design and are therefore areas of potential savings. The proposed tool will optimize network design for cost reduction in these categories. A review of the existing literature shows conflicting viewpoints and a lack of comprehensive evaluation on this topic.

Gray et al. [1] present an analysis of the effect on staff time of filling prescription orders from ADCs instead of a cart fill system. Time study data was incorporated in simulation models to compare systems of varying ADC and cart fill proportions. Gray concluded that ADC use should be minimized in order to reduce nurse labor and shift it to lower salaried pharmacy technicians. Gray, however, did not consider other effects of his claim as is evident in the writing of Chapuis [2] who argues that cart fill use should be minimized, in favor of ADC, because of its poor effect on prescription error frequency. Lathrop [3] presents results of a study that analyzed the effects of increasing the frequency of prescription fill rounds. Lin and others [4] analyzed the workflow implications of installing a prescription-filling robot in a central pharmacy. Thus far, a comprehensive and systematic approach for efficient hospital system design has not been presented. We aim to synthesize these and other ideas in a single, comprehensive decision-making tool. This paper establishes a set of cost components to be used in the tool.
Methods
A set of universally applicable variable characteristics was developed which can adequately describe hospital pharmaceutical distribution systems. Characteristics are general enough to accommodate hospitals of varying design yet comprehensive enough to satisfactorily and specifically define them. Specifying these variable values that describe the distribution system layout and the medication moving through it, enable calculation of transportation, facility, staffing, equipment, and inventory holding costs. Early models use user input of variable values to provide a total system cost and serve as an organizational structure for optimization models.

Distribution Framework
A common distribution framework provides the basis for variable determination and definition. The multi-hospital system is defined using a three-echelon inventory model where a centralized pharmacy provides storage for all hospitals, a pharmacy in each hospital holds inventory for use in that hospital, and ADCs provide storage space on patient units. Medication is shipped from the supplier to either the central warehouse pharmacy or a hospital pharmacy. Once in the hospital, there are two delivery options; cart fill and ADC. The cart-fill process involves centralized picking of patient prescriptions in either the central warehouse or hospital pharmacy. Order information is transmitted to the central location and a pharmacy technician picks the orders. On a regular basis (1-3 times daily), patient-specific prescriptions are delivered to inpatient units where they are stored to await nurse retrieval and subsequent administration. With ADCs, however, prescriptions are picked near the point of use, on the patient’s unit. Bulk medication comes from the warehouse or the hospital pharmacy and is stored in the ADC. When a prescription is ordered, a nurse picks the patient’s order from the cabinet and administers it to the patient. Thus, there are four main medication delivery pathways. Figure 1 shows the pathways. Note that this is not an exhaustive list of pathways. In the case of emergencies or stock outs, expedited trips from the warehouse or hospital pharmacy may be necessary; however, according to Geisinger Health System representatives, these types of orders only account for about 5% of medication deliveries. To maintain simplicity, the cost of these uncommon trips was accounted for by constants contained within cost calculations for the four main pathways instead of creating an additional expedited pathway.

Medication Classification
Two medication classifications, type and urgency, were defined in order to account for additional distribution costs and considerations. Three prescription urgency types, STAT, first dose, and maintenance dose, are characterized by the amount of allowable time for prescription delivery. Orders needed in 30 minutes or less are considered STAT orders. These are made when the patient is in immediate need of a specific medication. First dose is the initial dose of a particular medication to a patient and has an allowable delivery time of greater than 30 minutes. Recently admitted patients, or those starting a new medication, are typical
recipients of first doses. Every subsequent order after the first dose is a maintenance dose. As opposed to first doses and STAT orders, maintenance doses are scheduled in advance, typically with specific administration times.

Five medication types were defined based on unique characteristics which effect cost and storage locations. Controlled substances are highly regulated drugs that must be closely monitored. Compounds are drugs that require additional preparation by the nurse, such as cutting a pill in half to reduce the dose or crushing and mixing a pill with water to create a drinkable solution. IVs are relatively large bags used for intravenous medication administration that require more storage space than most medications. PRN (‘pro re nata’ or ‘as the situation demands’) meds are medications administered at the request of the patient such as pain relievers or cold medicine. Other pills are simply basic pills that do not meet the requirements of the previous classifications.

Model Description
The volume of medication through each pathway is the basis for cost calculation in the Excel model. The user enters the bed count for the hospital of interest and the model calculates an average daily prescription volume using a bed to prescription ratio extrapolated from historical Geisinger Health System data. The user then specifies the volume and classification of medication types in each pathway. It should be noted that the unit for a ‘script’ is a single dose (pill or other unit of medication).

The model is broken into four sections that represent the pathways. Each of the sections contain cost modules that use the pathway’s prescription volume to calculate the cost of a particular cost driver in that particular pathway. Table 1 shows the breakdown of pathway cost module assignments. Note that there is no reliable way to know the urgency of a medication’s administration before the prescription is made, but the probability of whether a medication will be ordered as STAT, first dose, or maintenance can be derived from historical hospital prescription data. Figure 2 shows a screenshot of the pathway volume section of the Excel model. The ‘% of medication type’ row is expected to contain fixed values that are specific to the hospital and depend on the nature of its patients’ needs. The lowest four rows, which are labeled with the pathway options will, in this case, be fixed and dependent on user entry. In future mathematical models, however, these values will be optimized.

Table 1. Pathways cost module assignments

| System-central cart fill       | Staff, inventory holding, order picking, transportation, facility |
| ADC centrally filled           | Staff, inventory holding, order picking, transportation, facility, ADC |
| ADC hospital filled            | Staff, inventory holding, order picking, ADC |
| Hospital pharmacy cart fill    | Staff, inventory holding, order picking |

Figure 2. Excel user data entry
The values included in Figure 2 are realistic options for prescription urgency and medication type pathway assignments. Due to increased effort, and therefore cost, of rushed or unexpected prescription orders, transportation distance should be minimized for expected STAT medications. Thus, ADCs are the ideal storage location since they are already near the patient. By the same logic, first dose will likely see a higher level of decentralization than maintenance doses. Medication type also plays a role in ideal pathway placement. For security reasons, controlled substances must be stored in ADCs. Considering labor cost, compounded substances and IVs that require manual preparation should be stored centrally where a lower salaried pharmacy technician will process the orders, instead of a nurse at an ADC. Storage of large IV bags should be where real estate is cheapest; the hospital or central pharmacy. Since PRN drugs are requested by the patient for his or her immediate use, they should be stored in the ADCs.

Cost Modules
Each Excel cost module is explained. Cost formulas are in the Variables and Formulas section.

Staff
Staff time to fill prescription orders depends on a number of factors. Storage location dictates who picks the medication, for example nurse time increases when medications are stored in, and thus picked from, the ADC. If the type of medication requires additional work such as with compounds, the picker’s time will increase with the additional preparation. Automation absorbs some workload from the staff who would otherwise be picking medication manually. Future data collection will quantify these factors. Calculated full time equivalent (FTE) values and wage information provided by the Bureau of Labor Statistics allow determination of an annual cost for each staff type. Note that driver FTEs are calculated in the transportation section and that staff wage information can be altered as needed by the user.

Transportation
Transportation can be performed by an internal courier or a third-party provider. The normal and expedited (to account for stock outs) trip cost for third-party providers is higher than with the internal couriers, while fuel, vehicle, and driver staffing costs are added in the internal option.

Robotic automation
This module accounts for the cost of automated order picking. Greater use of robotic picking causes a reduction in the staffing cost because the workload is absorbed by the robot. The user defines the percentage of scripts in each pathway that are automatically picked.

Inventory Holding
Using Geisinger Health System data, a relationship was identified between bed count and annual medication procurement cost. Each pathway, based on the prescription volume it handles, is assigned an annual procurement cost. Generally accepted inventory holding percentages range from 10–15%. Holding percentage assignments, 10% - warehouse, 13% - hospital pharmacy, and 15% - ADC, are based on the relative real estate values of the holding locations.

Facility
The facility module is a calculation of the warehouse cost. The up-front cost is a function of the footage price and the amount of medication held at any given time. A flat equipment cost is included to account for shelving, forklifts, or any other equipment required in the warehouse.

ADC
ADC cost is a function of ADC capacity and prescription volume in ADC pathways. It should be noted that ADC capacity, since drawers are broken into discrete sections, is more limited by the number of specific medications than the total volume of medication that it stores, however, this model only accounts for overall volume. Optimization models will consider specific medications. The cost of the ADCs is amortized over their useful lives.

Results
Development of a clear set of cost drivers and contributing variables has enabled the construction of the Excel model that will be used to explore various system designs and operating policies. It will provide a quick way to analyze the sensitivity of the system to changes in specific cost factors and serve as a basis for optimization models. Two models in particular manipulate variables identical to those in the Excel sheet; one minimizes cost and the other reduces missing doses. The output of these optimization models is a dataset that defines the variables. Related models include a capacitated network design model that, given the location of all hospitals in the system, determines the optimal location for a central warehouse. Another
model accepts vehicle capacity, a common beginning and end point, and the set of delivery locations to optimize transportation routing. This can be tailored to include transport frequency and incorporate expedited trips that could be run a variable number of times per day. Results, thus far, are composed of the framework for cost calculation and the related optimization models. The next step is populating these models with relevant data to test and verify their effectiveness.

Discussion
This work serves to organize the system of hospital pharmaceutical distribution in a universally applicable way. By exploring the various cost components discussed, one can arrive at a reliable estimation of the distribution cost for the system. Furthermore, as an organization of the cost components, it lays the groundwork for optimization tools. A major shortcoming of this research is the lack of verifiable results. Data collection has been hindered by a number of factors thus preventing the construction of useable models. Time studies, to be performed at Geisinger Health System facilities, will provide a basis for the accurate definition of distribution costs in various pathways as well as a better understanding of staffing time requirements.

Conclusion
The strategic design of pharmaceutical distribution systems has the potential to significantly reduce hospital operating costs. Simulation models, like the Excel, will enable evaluation of the various design alternatives, and optimization models will determine which alternative is best. Inclusion of future data collection in the already constructed model framework will create a valuable tool for healthcare professionals.

Acknowledgments
Thank you to the Swanson School of Engineering and the Office of the Provost for partial funding of this research. Also, thank you to Dr. Bryan Norman for mentoring the project and providing partial funding.

References
### Variables and formulas

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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$t_{ipm}$</td>
<td>Time for staff member type $i$ to pick a prescription in pathway $p$ of medication type $m$</td>
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<td>$s_p$</td>
<td>Prescription fills per day in pathway $p$</td>
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<td>$w_i$</td>
<td>Annual wage for staff member type $i$</td>
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<tr>
<td>$c_s$</td>
<td>Capacity of space $s$ (courier - scripts/vehicle, robot – scripts/day, ADC – scripts/ADC)</td>
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<tr>
<td>$f_t$</td>
<td>Cost per trip of courier type $t$</td>
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<table>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$E_t$</td>
<td>Cost of an expedited trip for courier type $t$</td>
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<td>$x$</td>
<td>Probability of expedited trips</td>
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<td>$A_e$</td>
<td>Amortized annual cost of item $e$</td>
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<tr>
<td>$T$</td>
<td>Annual number of inventory turns</td>
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<td>$P_p$</td>
<td>Annual procurement assigned to pathway $p$</td>
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<td>$h_p$</td>
<td>Holding cost % at location $p$</td>
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<td>$p_s$</td>
<td>Cost per square foot of floor space in storage location $s$</td>
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<td>$g$</td>
<td>Required space for an individual prescription unit</td>
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<td>$e$</td>
<td>Warehouse equipment cost</td>
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<tr>
<td>$A$</td>
<td>Up front cost of an ADC amortized over its useful life</td>
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</table>

### Staffing

Annual staffing cost = $\sum_{i,p,m} t_{ipm} \left( \frac{s_p}{8 \text{ hours}} \right) \times w_i$

### Transportation

- Annual transportation cost ($3^{rd}$ party) = $\sum_p \left( \frac{s_p}{c_{3rd\ party}} \right) \times f_{3rd\ party} + E_{3rd\ party} \times x$
- Annual transportation cost (internal courier) = $\sum_p \left( \frac{s_p}{c_{internal}} \right) \times f_{internal} + E_{internal} \times x + A_{vehicle}$

### Robotic automation

Annual robotic order picking cost = $\sum_p A_{robot} \times \left( \frac{s_p}{c_{robot}} \right)$

### Holding cost

Annual holding cost = $\sum_p \left( \frac{P_p}{T} \right) \times h_p$

### Facility

- Up front cost of warehouse = $\sum_{p=1,2} \left( \frac{P_p}{T} \right) \times g \times p = W$
- Annual facility cost = $W$ [amortized over useful life] + $e$

### ADC

$\sum_{p=3,4} \left( \frac{s_p}{c_{ADC}} \right) \times A$
Computational Modeling of Wall Stress in Ascending Thoracic Aortic Aneurysms with Different Valve Phenotypes

Thomas G. Kappila, Joseph E. Pichamuthu, Justin S. Weinbaum, Julie A. Philippi, Thomas G. Gleason, and David A. Vorp

Abstract
Ascending aortic thoracic aneurysms (ATAAs) affect about 15,000 people annually in the United States. Formation of the ATAA is associated with the stiffening and weakening of the aortic wall, leading to potential rupture or dissection. Bicuspid aortic valve (BAV) is the most common congenital heart malformation, occurring in 1% to 2% of the population, compared to the normal tricuspid aortic valve (TAV). The goal of the study was to evaluate the spatial variation in wall stress between BAV and TAV ATAAs. Virtual 3D geometries of thoracic aortas were reconstructed from pre-operative computed tomography (CT) scans of patients. The aorta was modeled as a shell of a homogenous, nonlinear, isotropic, hyper-elastic, and incompressible material with a uniform thickness and under a constant pressure of 120 mmHg. Material properties were specific to either BAV or TAV patients, using values obtained from prior work of this lab. From the data collected, on average, BAV patients had a higher mean wall stress than TAV patients, but peak wall stress was not significantly different. The location of peak stress was consistent between TAV and BAV patients.

Keywords: Ascending thoracic aortic aneurysms, bicuspid aortic valve, tricuspid aortic valve, computational modeling

Introduction
Ascending thoracic aortic aneurysms (ATAA) affect about 15,000 people annually in the United States [1]. Aneurysm formation is associated with the stiffening and weakening of the aortic wall, leading to potential rupture [2]. Weakening of the wall occurs as a consequence of medial degeneration, deriving from apoptotic loss of smooth muscle cells and fragmentation of elastin and collagen fibers. Once the ascending aorta’s diameter reaches 6.0 cm, the risk of rupture or dissection becomes 31%, therefore normal surgical intervention for ATAAs is suggested once the diameter of the aorta reaches 5.5 cm [3]. Bicuspid aortic valve (BAV) is the most common congenital heart malformation, occurring in 1% to 2% of the population. Studies have shown that patients with different valve morphologies have different material properties for the ascending aorta [4]. Dissection and rupture are biomechanical phenomena occurring when the aortic wall stress, due to hemodynamic factors, exceeds local wall strength. Hence, the goal of the study was to evaluate the spatial variation in wall stress between BAV and TAV ATAAs.

Methods
3D Reconstruction
Anonymized computed tomography (CT) scans of patients with ATAA under surveillance for aortic dissection and rupture were obtained for this study. Virtual 3D aortic geometries were reconstructed from pre-operative CT scans of patients (n=19) undergoing elective surgery (after IRB approval). This scan generally occurred a week or two before surgery.
took place. The CT scan images were first loaded into Mimics 15 (Materialise, Plymouth, MI), where pixel thresholding was applied to identify aortic and lumen boundaries, allowing for the creation of a coarse 3D volume of model of the ATAA. The model was exported as a point cloud after initial smoothing for further processing into Geomagic 2013 (3D Systems, Rock Hill, SC), where the model was further smoothed and patched. The model was exported for the use of finite element analysis, using non-uniform rational B-splines (NURBS) to represent the surface geometry.

**Finite Element Analysis**

The reconstructed ATAA wall surface geometry was then meshed and discretized into finite elements in Abaqus 6.13 (Dassault Systèmes, Waltham, MA). The ATAA was modeled as a shell of a homogeneous material with a uniformly distributed thickness of 2.25mm. The wall was considered nonlinear, isotropic, hyper-elastic and incompressible, and under a constant pressure of 120 mmHg. The strain energy function (W) used was previously reported by our group for BAV and TAV:

\[ W = \alpha(I_1 - 3) + \beta(I_1 - 3)^2 \]  \hspace{1cm} \text{(Equation 1)}

In this function, \( \alpha \) and \( \beta \) are model parameters (in N/mm\(^2\)) characteristic of the tissue’s material properties and \( I_1 \) is a strain invariant. The model parameter set \([\alpha, \beta]\) was \([0.0465, 0.152]\) for BAV models and \([0.065, 0.955]\) for TAV models [4]. The output of our computational modeling was a stress map across the wall surface. The schematic of the work flow is seen in Figure 1.

**Data Processing**

The measure of transmural wall stress used is the “equivalent” or von Mises stress, which is frequently used to describe the stress field of materials under multi-axial loading conditions. The peak wall stress (PWS) is defined as the maximum von Mises stress acting within the ascending aorta (the region starting at the aortic valve and immediately before the brachiocephalic artery, seen circled in red in Figure 1, image F), while mean wall stress (MWS) was defined as the mean von Mises stress value within the same region. Both MWS and PWS of the ascending aorta were calculated, and a two sample, independent, one-tailed t-test was performed to evaluate the differences between TAV and BAV. A 95% confidence interval (95%CI) was also calculated from the data.

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**Figure 1. Methodology Schematic**

Models were created through the process of CT reconstruction (A), exporting a point cloud out of Mimics software (B), smoothing and cleaning in Geomagic (C), meshing in Abaqus 6.13 (D), with the final map of von Mises stress from the FEA conducted in Abaqus 6.13 (E). The color scale in (E) indicates areas of high stress in red, and areas of low stress in blue. (F) shows the ascending aorta, circled in red, used in the calculation of PWS and MWS. This region starts at the aortic valve, and ends immediately before the brachiocephalic artery.
Results
At the time of elective surgery, the average MWS in BAV patients (17.3±2.0 N/cm², 95%CI [15.8, 18.7]) was significantly higher than the average MWS in TAV patients (15.0±2.2 N/cm², 95%CI [13.3, 16.7]), with p=0.016. However, the difference in mean PWS between TAV patients (30.9±8.4 N/cm², 95%CI [28.1, 36.8]) and BAV patients (32.4±6.0 N/cm², 95%CI [24.4, 37.4]) was not statistically significant. Values given here represent mean±standard deviation. A 95%CI plot of the stress data is shown in Figure 2, and additional data is reported in Appendix 10.1.

The location of peak stress within the ascending aorta was consistent between BAV and TAV groups, with the maximum wall stress localized above the left coronary artery, as seen in Figure 3. The area of peak stress (shown in red) occurs in the lower half of lesser curvature of the ascending aorta, above the left coronary artery (indicated with a white asterisk).

Discussion
The results from the study indicated a difference in stress within the aortic wall between the valve morphologies, but no difference between the two valve types when looking at the location of peak stress.
stress within the ascending aorta. While the peak wall stress was equivalent between the two valve morphologies, the mean wall stress was different, perhaps indicating the differences in the growth and remodeling of ATAs. Taken into account with the low p-value (0.016), the data indicated that the average BAV patient’s ascending aorta experiences 12.9% more mean wall stress than the average TAV patient. However, as demonstrated through the mechanical testing of excised BAV and TAV tissue, BAV aortic valve tissue has a greater tensile strength than TAV tissue [4]. Because BAV tissue is stronger than TAV tissue, judgments concerning relative risk of dissection and rupture between TAV and BAV ATAA patients could not be made on this data alone.

The work done here aligns with, and adds a new element to, the existing research done in computational modeling of ATAs. As shown by Krishnan et al, utilizing a MRI based aortic reconstruction, and developing patient-specific material properties using an inverse analysis based on measured aortic wall strain to calculate material parameters, the range of peak stress within the model there aligned with the method used here [5]. In addition, as shown by Pasta et al, the blood flow profile of BAV and TAV individuals with ATAs are significantly different, creating more stress within the BAV patient [6]. Finally, Trabelsi et al was able to create a computational model of the ascending aorta, using material properties taken from tissue excised during elective surgery [7]. Here again, the range and location of stress within the model corroborated with the model here. The work done here aligns with the previous research, and improves on current work by analyzing both a greater number of patients. The current methodology of aortic catastrophe risk assessment through the measure of aortic wall strain has been shown as a poor indicator of risk [8], and as such, the development of a more accurate, non-invasive risk assessment tool is required. Further development into patient-matched model creation and analysis could provide the more accurate prediction model.

The research done here provides multiple avenues for future exploration. First, the computational model could be advanced by including the blood pressure at the time of scan (instead of assuming maximum normal physiological conditions), as it would more accurately characterize patient stress, especially considering patients at risk for rupture and dissection will have non-normal flow pressure and patterns. Second, a regular scan schedule, with a set time between scans, would allow for the accurate tracking of aortic wall degeneration, providing researchers with vital rate of change of stress data. While helpful, this method of testing is cumbersome in a normal population due to issues with patient participation, as it would force the patients to undergo an additional amount of testing that may not be medically necessary, and be exposed to an excess of radiation. Controlling for unaccounted variables would also improve the study, as stratifying our groups through variables such as gender and age would add a new dimension to the study, potentially teasing out differences between these patient groups.

**Conclusion**

There is an increase in the mean wall stress within the ascending aorta for BAV patients, when compared to TAV patients. However, the value of peak stress between the two valve morphologies was not significantly different. Similarly, the location of peak stress was consistent between both valve types, located above the left coronary artery. While the data did show a real difference in aortic wall stress between the two valve morphologies, the data also indicated large similarities between the two morphologies, and emphasized the need for more thorough testing, especially through the use of more patient-specific material properties, and the inclusion of patient-specific blood flow patterns.

**Acknowledgments**

Patient images were obtained from the Department of Cardiovascular Surgery, University of Pittsburgh Medical Center. Funding was provided through the Swanson School of Engineering.
References


Appendices
Results
Patients with a BAV (n=10) had a mean wall stress (MWS) ranging from 14.2 N/cm² to 21.0 N/cm², and patients with a TAV (n=9) had a MWS ranging from 10.2 N/cm² to 17.6 N/cm². Similarly, BAV patients had a peak wall stress (PWS) between 23.6 N/cm² and 45.6 N/cm², while TAV patients had a PWS ranging from 19.0 N/cm² to 48.9 N/cm². For BAV patients, the standard error of the mean was [0.6, 1.9], for MWS and PWS, respectively, while TAV patients had a standard error of the mean of [0.7, 2.8], for MWS and PWS, respectively. The difference between BAV and TAV MWS and PWS was 2.2 N/cm² and 1.5 N/cm², respectively.
Black Silicon for Photovoltaics and Antibacterial Surfaces
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Abstract
Black silicon, named as such because of its black appearance to the naked eye, can be more accurately described by characterizing the geometrical properties of silicon nanostructures fabricated on its surface. Fabrication control of nanostructures varied, producing geometries ranging from high aspect ratio nanoneedles to pyramidal nanostructures. The purpose of this study is to understand how altering the geometrical properties of silicon nanostructures impact the antireflective and antibacterial properties the material. Antireflective properties are of interest in order to reduce incident light reflectance for solar cells, while bactericidal properties are compelling for antibacterial surfaces and coatings.

The morphology of fabricated nanostructures was studied as a function of parameters internal to the inductively coupled plasma reactive ion etching (ICP RIE) process, using \( \text{SF}_6 \), \( \text{O}_2 \), and \( \text{C}_4\text{F}_8 \) as reactive ion sources. Successful nanostructures geometrically consistent with those of established black silicon products were observed to uniquely originate from unmasked silicon through a self-organizing mechanism. Likewise, variations of black silicon nanostructures were found to be geometrically similar to known antibacterial surfaces. Black silicon was shown to have antireflective properties in the wavelength ranges from 200 to 800 nm and to be a hydrophobic surface.

Keywords: Black silicon; Antireflective; Antibacterial

Introduction
Silicon-based solar cell efficiency is limited by silicon’s high reflectivity, where typically over 30% of incident light is reflected. Minimizing the amount of reflected light serves to maximize the amount of absorbed photons in the silicon semiconductor, thus increasing the quantity of excited electrons per unit of incident light. This creates a more dense electric current across the cell’s p-n junction, leading to an overall increase in the cell’s power conversion efficiency [1].

Anti-reflective coatings, such as silicon nitride, are currently the most commonly used method to reduce light reflectivity. However, nanotechnology has emerged as a promising solution toward reducing reflectivity at a lower cost. Fabricated arrays of repeating geometrical subwavelength nanostructures, such as columns, wires, cones and pyramids, on the surface of silicon have been shown to possess light trapping abilities via enhanced light scattering within the array [2].

These nano-arrays are typically patterned by a pathway combining various processes such as RIE, plasma enhanced chemical vapor deposition, lithography, evaporation, etc. These patterning mostly involve prefabricated masks, which serve as templates for etching and deposition processes. Fabricating both the masks and the arrays involve multi-step synthesis—expending valuable time and expensive resources with each step [2].

Due to the same geometrical principles governing the light trapping effects seen in other nano-arrays, black silicon nanostructures exhibit low incident light reflection (below 2% in the visible light wavelength range) [3]. This low reflectivity explains why the silicon appears black, as a near-absent amount of
visible light is reflected to the human eye. In addition, black silicon has been shown to absorb light in the near infrared wavelength range (up to 1000 nm), a property that silicon nitride coated cells do not possess [3]. In contrast to costly conventional methods, black silicon morphology has been shown to occur through a unique self-organizing and mask-less process, avoiding many inherent production costs to other incident light absorption-enhancing processes [3][4].

The nanostructures on black silicon’s surface are quite similar to known superhydrophobic surface conditions, which create a self-cleaning effect such that bacteria are repelled from the surface topography and ultimately impedes bacterial attachment [5]. Furthermore, black silicon characterized by closely-packed, high aspect ratio nanopillars has been observed to mechanically lyse Gram positive and Gram negative bacteria cell walls and membranes [6].

**Methods**

**ICP RIE**

A Surface Technology Systems Multiplex ICP RIE device was used to fabricate black silicon. A 600 W power supply applied through the ICP RIE’s RF inductive coil generated high-density plasma, which was derived from etchant and passivation gases flowing through the coil. Using the Bosch process DRIE model, etchant and passivation plasmas were generated separately in two alternating cycles. Next, etchant and passivation components from their respective plasmas were accelerated with high ion energy towards the silicon substrate by applying an RF bias at the backside of the substrate. This backside power source controlled ion directionality and acceleration toward the surface. More specifically, the substrates were phosphorous doped (p-type), <100> oriented, 4” round silicon wafers.

During the etch cycle, SF$_6$ and O$_2$ gases were simultaneously implemented in the ICP RIE chamber. In contrast, C$_4$F$_8$ was the sole gas implemented during the passivation cycle. The RF bias was set at 20 W for every etch cycle and 0 W for every passivation cycle. The etchant gas flow rates and duration of etch cycle were also kept constant. During 9-second etch cycles, SF$_6$ flowed at 130 sccm, while O$_2$ flowed at 13 sccm.

**ICP RIE variables and sample characterization**

The rate of C$_4$F$_8$ gas flow, passivation cycle time, and total cycles were studied independently for their effect on the geometrical properties of silicon nanostructures. Sensitive convergence of ICP RIE parameters towards feasible reaction conditions produced three significant ICP RIE “recipes,” as highlighted in Table 1. These recipes were deemed to be significant due to visual observation and SEM characterization of the samples they produced.

A camera phone was used to visually observe and record every sample. Visual observations such as color and presence of a reflection on the sample gave important insight when fine-tuning the ICP RIE recipe. Visual observation also was key for observing the relative hydrophobicities of the samples. This was done by qualitatively comparing water contact angles from side-view images. SEM characterization was performed on a Philips FEI XL-30F SEM to record geometrical measurements of mean depth and mean pitch. Depth was defined as the vertical etch distance. Pitch was defined as the center-to-center distance between neighboring nanostructures.

**Sample analysis for % reflection**

Optical spectroscopy was used to measure the percentage of incident light that was reflected upon projection toward black silicon samples. The optical spectrometer used was capable of measuring reflectance in the wavelength range from 200 to 800 nm. The samples, and thus associated ICP RIE recipes and geometrical properties, were then ranked based on antireflective effectiveness.

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**Table 1. ICP RIE independent variables and values for Samples 1, 2, and 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_4$F$_8$ Flow (sccm)</th>
<th>Passivation Time (sec)</th>
<th>Number of Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>14</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>14</td>
<td>80</td>
</tr>
</tbody>
</table>
Sample analysis for bacterial viability

*S. epidermidis* bacterial viability is currently in the process of experimental design and implementation. *S. epidermidis* will be incubated over black silicon samples, and bacterial cell counts at various incubation periods will be recorded. The samples, and thus associated ICP RIE recipes and geometrical properties, will then be ranked based on bacterial killing effectiveness.

Results

Of the 34 samples that were fabricated, three distinct geometrical results were achieved, chronologically named Samples 1, 2, and 3. Other samples were either insignificant or closely related to the geometrical structure of Samples 1, 2, or 3. The characteristic structure of Sample 1 was a high depth and low pitch, an intermediate depth and higher pitch for Sample 2, and a low depth and higher pitch for Sample 3. These descriptions are quantified in Table 2 and visualized in Figure 1.

### Table 2. Mean depth and pitch of nanostructures for samples 1, 2, and 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Depth (μm)</th>
<th>Mean Pitch (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.01</td>
<td>450</td>
</tr>
<tr>
<td>2</td>
<td>2.994</td>
<td>722</td>
</tr>
<tr>
<td>3</td>
<td>0.784</td>
<td>738</td>
</tr>
</tbody>
</table>

### Figure 1. The appearance of black silicon to the naked eye versus under SEM characterization. Sample 1 is seen by the naked eye in A, and under SEM characterization in B (scale bar = 5 μm). Sample 2 is seen by the naked eye in C, and under SEM characterization in D (depth measurements shown as well). Sample 3 is seen by the naked eye in E, and under SEM characterization in F (scale bar = 1 μm).
Sample 3 was qualitatively determined to have the best antireflective properties, followed by Sample 2 because they were darkest to the naked eye. Reflectivity measurements were not taken on Sample 1 because of the observed brown color. Sample 3 reflected less than 5% of incident light across most of the visible light range, as shown in the reflectance spectra of Figure 2. Sample 2 showed similar results, reflecting less than 7% across the spectrum.

Sample 1 was visually determined to be comparatively more hydrophobic than Sample 3, as shown in Figure 3.

**Discussion**

The maskless, self-organization morphology of black silicon is truly unique to the fabrication of nanostructures on silicon surfaces. The mechanism for the initiation of this process is not fully understood, but it is thought to occur due to an imperfect distribution...
of either the ICP RIE-generated plasma or the silicon wafer thickness, creating an uneven initial passivation, followed by electric loading at these sites and subsequent uneven etches [4]. These first few cycles effectively create multiple initiation sites, evidenced by small “bubbles” or “pits,” as observed in Figure 4.

Under the RF power source, SF$_6$ gas is separated into fluorine radicals that primarily etch the silicon surface at a high etch rate. The ionized silicon-fluoride etches byproducts then react with oxygen radicals to form silicon oxyfluoride, which acts to protect the sidewalls of the nanostructures [3]:

This protection creates undulating sidewalls, with one undulation for each etch cycle. This ultimately allows for stable high aspect ratio structures to form after many cycles. These high aspect ratio nanostructures realized by DRIE during the propagation phase are not observed in conventional RIE systems [7].

**Conclusions**

In essence, all of the ICP RIE parameters work together in complex ways such that black silicon morphology is difficult to predict while altering more than one parameter at a time. This also led to difficulty in creating an optimal ICP RIE recipe. Although the complete mechanism of black silicon morphology is unknown, some correlations between varying parameters and the morphological outcome can be concluded. Increased treatment time, determined by the total number of cycles, always lead to an increase in the depth of the nanostructures. This is simply due to an increased total time of vertical etching by SF$_6$. Increased passivation cycle time lead to an increased pitch, except for when passivation time extended beyond 14 seconds, which caused overpassivation and the lack of consistent nanostructures. Decreasing the C$_4$F$_8$ flow rate caused an overall decrease in uniformity of the samples, but also correlated with thicker, pyramidal nanostructures and reduced reflectivity.

It can be concluded that Sample 3’s distinct geometries align well with the purpose of antireflective surfaces. This is based on reflectivity measurements below 5% and geometrical similarities with known antireflective surfaces, whereas black silicon is more favorable because of ease and cost of fabrication.

**Acknowledgments**

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**References**


A Simple, Efficient, and Transferable Approach for High-Yield Separation of Nanoparticles

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Abstract
Nanoparticles offer fascinating new possibilities to tailor material properties and develop novel, more sustainable and efficient industrial processes. However, the recovery of very small nanoparticles (<10 nm) during synthesis and their subsequent deposition onto supports is challenging, costly, and time consuming. We have developed a quick and efficient salt recrystallization method by which stable nanoparticles can be recovered from solution, deposited onto supporting material, and protected against thermally induced growth. We demonstrate the utility of this method by separating 6 nm silica (SiO2) from solution using NH4Cl and depositing 4 nm platinum (Pt) onto silica supports using NH4HCO3. In each case, almost complete recovery of nanoparticles was achieved. This general approach to nanoparticle recovery is not only transferable to different salt/nanoparticle combinations, but also improves synthesis efficiency and can lead to more versatile production methods.

Keywords: Nanoparticles; Recovery Techniques; Membrane Centrifugation; Salt Recrystallization

Introduction
Nanomaterials are used in a wide range of applications, including pharmaceuticals [1], optics [2], coatings [3], and catalysis [4], because their small size often results in unique material properties that are fundamentally different from their bulk counterparts [5]. This has motivated the development of a wide range of synthesis procedures that produce nanoparticles (NPs) with the desired size and the required high degree of precision [6]. In most of these syntheses, so-called “capping agents” are used to achieve low polydispersity and high control of particle size and shape. Their long polymer chains surround NPs that form in solution and will inhibit growth of particles beyond a desired size [7]. However, NPs that are protected by capping agents are extremely stable in solution as a result of steric repulsion between polymer chains, which prevents NPs from interacting with one another [8]. Therefore, NPs protected by capping agents are not easily recovered from their synthesis broth. Particularly, for very small NPs (<10 nm), extensive centrifugation with the aid of a membrane filter is required in order to remove these NPs from solution, which is very time and energy consuming. This approach is especially problematic when synthesizing practical sample sizes (i.e., in excess of “academic” lab-scale samples of a few 100 mg) due to filter clogging and time constraints.

Furthermore, many applications require the subsequent removal of the capping agents in order to make the NP surface accessible and hence functional. This removal typically requires high temperature thermal treatment, or calcination, which often results in sintering of the NPs (i.e. in their agglomeration) and hence in loss of the carefully controlled NP size.

Chen et al. recently reported that such sintering of ~4 nm Pt,Fe NPs during high temperature calcination can be avoided by embedding the particles in KCl [9]. However, this procedure can be accomplished only with the use of metal-chloride precursors (e.g., PtCl4) and not all synthesis procedures use metal-chlorides. Therefore, the procedure described by Chen et al. is very limiting and is not transferrable to procedures that do not use metal-chlorides.

Here, we present a novel approach based on “salt recrystallization” as a more transferable and general method of NP recovery. The method by Chen et al. certainly recrystallizes KCl to recover their nanoparticles, but it requires KCl recrystallization...
to work and can be used only for specific systems. Our method is general and can be used to recover NPs that do not at all require salt recrystallization for their recovery, but would otherwise require expensive and time consuming recovery techniques. Salt recrystallization is the process by which the complementary ions of a salt dissolved in a solution begin to recompose themselves and recrystallize under the influence of temperature or the presence of a solution in which the salt is insoluble. These crystals then go on to “catch” the desired NPs, which allows for easier separation. We demonstrate that salt recrystallization can significantly simplify and shorten NP recovery procedures as well as the deposition of NPs onto supports by circumventing the required membrane centrifugation without affecting the yields and size distributions of the recovered NPs. Additionally, embedding NPs in thermally stable salts can mitigate particle growth and agglomeration even beyond the decomposition temperature of typical capping agents.

Methods

Synthesis of 6 nm silica
Silica NPs, 6 nm in diameter, were synthesized using a two-phase variation of the Stöber method. Briefly, a catalyst stock solution was prepared by mixing ammonia with deionized (DI) water to a pH of 11.4. Next, 2.6 g of tetraethyl-orthosilicate (TEOS) was diluted in 5 ml ethanol, mixed thoroughly, and added to 34.75 g of catalyst stock solution. The solution was then stirred for 3 hours at 60 °C.

Synthesis of Silica Support Materials
Silica supports, approximately 120 nm in diameter, were synthesized using the conventional Stöber method. A solution containing 18 mL of TEOS, 99 mL of DI water, 36 mL of ammonium hydroxide (30% by volume), and 65 mL of ethanol (190 proof) was mixed at room temperature for one hour. The resulting white solid was separated from the solution via centrifugation.

Synthesis of platinum nanoparticles
Pt NPs (3–5 nm in diameter) were synthesized from a solution containing 1.25 mL of 10 mM chloroplatinic acid aqueous solution and 2.5 mL of 1.39 mM polyvinylpyrrolidone (PVP, ~ 10,000 molecular weight) aqueous solution at 0 °C, which was stirred until well mixed. Next, 1.25 mL of 0.1 M sodium borohydride aqueous solution was added rapidly. The solution was left to react for 30 minutes. When using the conventional method of NP separation, the NPs were then recovered using membrane centrifugation (Centricon Ultracel-10K, Amicon Ultra Inc.).

Conventional synthesis of Pt/SiO₂
Pt NPs were synthesized as described above. After washing, the Pt NPs and 240 mg of (120 nm) silica support were dispersed in 2 mL of DI water. The solution was stirred for one hour at room temperature and then dried in vacuum at 100 °C. The resulting Pt/SiO₂ sample was then calcined at 300 °C to remove PVP.

Characterization of nanomaterials
Transmission electron microscopy (TEM) images were taken on a JEOL JEM2100F with an accelerating voltage of 200 keV. Sizes of NPs were determined using ImageJ with TEM images from particular samples. From these, the mean and standard deviation were then calculated.

Nanoparticle separation via salt recrystallization
Salt was added to the solution containing NPs until the solution was saturated. Liquid in which the salt is insoluble was then rapidly added to the solution and agitated to accelerate precipitation. The resulting precipitate and NPs were then recovered via conventional centrifugation. Finally, the salt was removed via calcination in air. Ammonium chloride salt was used to recover silica NPs and ammonium bicarbonate and potassium chloride salts were used to recover platinum NPs.

Results and Discussion

Separation of 6 nm silica
The presence of surface hydroxyl groups on the silica NP surface renders these particles highly stable in the basic synthesis solution environment, and hence makes their recovery difficult. The hydrogen ions on the hydroxyls dissociate, which results in the oxygens being negatively charged and strong electrostatic repulsive forces between particles. This repulsion between particles is what prevents them from collecting after conventional centrifugation. Their high stability in solution necessitates the use of membrane centrifugation for their recovery.

Membrane centrifugation, while effective, is a tedious, time-consuming, and inefficient process. Membrane centrifuge tubes are typically very small. In our case, each tube only held 15 mL of solution, but the synthesis of 6 nm silica results in 43 mL solution and
700 mg of solid particles. This synthesis took three hours to complete. Since centrifugation time is directly related to solution volume, the solution was distributed into four membrane centrifuge tubes to speed up the recovery, which took a total of three hours to complete, resulting in a total preparation time of six hours. Furthermore, high concentrations of solids often cause membrane fouling, which interrupts the centrifugation process. The materials were then dried and calcined at 500 °C to remove any residual TEOS.

As an alternative approach, 6 nm silica NPs were recovered from solution using salt recrystallization. Once the synthesis of the particles was complete, which took three hours, ammonium chloride ($\text{NH}_4\text{Cl}$) salt was added to saturate the solution. After reaching the saturation point, which took approximately five minutes, ethanol was rapidly added upon stirring to reduce the solubility of $\text{NH}_4\text{Cl}$ in solution and initiate recrystallization of the salt. This solution was then separated into two 50 mL (conventional) centrifuge tubes, instead of four 15 mL membrane centrifuge tubes, and centrifuged for 20 minutes with three ethanol washes in between, resulting in a total preparation time of 205 minutes.

The recovered solid contained—beyond $\text{NH}_4\text{Cl}$ and silica—residual TEOS, which needed to be removed via calcination (at ~500 °C). This calcination step simultaneously also removed the $\text{NH}_4\text{Cl}$, which decomposes to ammonia ($\text{NH}_3$) and hydrochloric acid (HCl) at temperatures above 338 °C. Using a salt with a decomposition temperature higher than 500 °C would have required more heating than necessary to recover the NPs, which was avoided by using $\text{NH}_4\text{Cl}$. It should be noted that the $\text{NH}_3$ and HCl fumes could be captured and condensed at room temperature and then reused, further reducing the amount of waste. Overall, this new procedure reduces the amount of time required to prepare silica NPs by 43% and avoids the use of membrane centrifuges, which are costly and have limited lifetimes. The salt method resulted in a 90% silica yield, which is identical to the yield using membrane centrifugation, and produced particles with an average size and size distribution indistinguishable from those obtained using membrane centrifugation, as shown in Figure 1.

**Figure 1.** TEM images of silica NPs separated using (a) membrane centrifugation and (b) our salt recrystallization method. (c) NP size distributions taken from TEM images, from which the mean and standard deviation were calculated from particle diameters determined using ImageJ. NP diameters, for conventional ($N=249$) and salt method ($N=167$) were 6.18 ± 0.69 and 6.18 ±0.74 nm, which are both respectively represented on the graph by the error bars.
Deposition of platinum catalyst onto silica support

To test the flexibility of the new separation approach, we applied the salt recrystallization method to the recovery of platinum NPs, which were intended for use as catalysts and hence had to be supported on silica supports (now formed by large silica particles of ~120 nm). Platinum NPs were stabilized during synthesis using a capping agent (“PVP”) in order to prevent agglomeration during the synthesis and deposition steps. Similar to the 6 nm silica, this stability makes recovering them from solution a difficult task beyond the limits of conventional centrifugation. Membrane centrifugation can successfully separate the particles, but, again, at the expense of much time and energy. The total time it took to recover the platinum NPs from solution with the aid of membrane centrifugation was two hours. Their subsequent deposition onto silica supports, as described in Section 2.4, took one additional hour to complete.

In order to demonstrate the versatility of the salt recrystallization method, ammonium bicarbonate (NH₄HCO₃) was used instead of NH₄Cl. With a very low decomposition temperature of 41.9 °C, NH₄HCO₃ requires far less energy to remove than NH₄Cl. This low temperature allows for the PVP to remain intact so that the platinum NPs do not agglomerate before their deposition onto silica. In this case, a different salt was chosen not because a different NP was being recovered, but because the procedures were different. Silica NPs can handle temperatures above 338 °C (the decomposition temperature of NH₄Cl) in their preparation, but platinum NPs surrounded by PVP cannot. The PVP would decompose by that temperature and the NPs would agglomerate before they deposit onto the 120 nm silica supports.

As before, the platinum NPs were synthesized and then sufficient NH₄HCO₃ was added to saturate the solution. The 120 nm silica support particles were

Figure 2. Representative TEM images of Pt/SiO₂ using (a) the conventional method and (b) the salt method. (c) NP size distributions taken from TEM images, from which the mean and standard deviation were calculated from particle diameters determined using ImageJ. NP diameters were (a) \( N = 87 \) 4.1 ± 1.0 and (b) \( N = 166 \) 4.3 ± 1.0 nm, which are both respectively represented on the graph by the error bars.
dispersed in isopropanol and then rapidly added to the synthesis bath and agitated. The solution was then centrifuged to give a dark solid, which was then dried in a vacuum oven at 60 °C to decompose the salt. The Pt/SiO₂ mixture was then briefly mechanically mixed using mortar and pestle and the sample was calcined at 300 °C to remove the PVP.

As for 6 nm silica, the recovery procedure for platinum NPs and their subsequent deposition onto silica supports were significantly shortened by the salt recrystallization approach. Both syntheses for platinum NPs took 60 minutes, with the salt method adding an extra five minutes to dissolve the salt in the synthesis solution. In contrast with the conventional method, the salt method only consumed 20 minutes for centrifugation and did not require an hour for deposition onto silica supports. Membrane centrifugation was avoided and the number of steps required to prepare platinum NPs on silica was reduced. While the conventional method requires a wet deposition step for platinum deposition onto silica, followed by drying of the sample, the salt method only requires the sample to be dried following NP recovery in order to produce supported platinum NPs. The conventional method resulted in a total time of four hours as opposed to 85 minutes for the salt method. Both conventional and salt recrystallization methods result in the same average NP size and size distribution. Furthermore, energy dispersive X-ray spectroscopy (EDX) confirms similar weight loadings of 0.68 and 0.64 wt% Pt achieved using conventional and salt methods, respectively. Analysis of TEM images for platinum on silica prepared conventionally and using the salt method is displayed in Figure 2.

**Protected annealing of 2.5 nm platinum**

As mentioned above, protective capping agents require thermal decomposition to be removed from the NP surface, which often results in undesired particle growth. Embedding NPs in a thermally stable salt has been shown to prevent particle agglomeration at high temperatures [9]. To demonstrate this stabilization for the current approach, platinum NPs were recovered from solution using potassium chloride (KCl), which has a very high decomposition temperature of 778 °C. NH₄Cl and NH₄HCO₃ would have decomposed well below this temperature and would not have been able to protect the NPs from agglomeration. The KCl/Pt solid mixture was then calcined at 500°C for two hours. However, Figure 3 shows that this approach, initially,

![Figure 3. TEM images of 2.5 Pt NPs from undiluted synthesis solution (a) before and (b) after 500°C calcination, showing particle growth.](image)
did not prevent particle growth. We hypothesize that the individual platinum NPs were not sufficiently separated in the KCl matrix and thus were able to agglomerate based on small residual mobility of the particles. This also shows how much the platinum NPs grow at 500°C when not sufficiently protected.

In order to test that hypothesis, the synthesis solution for platinum was diluted with DI water in order to reduce NP density and hence better separate the particles from each other. The particles were then, again, recovered from solution using KCl and calcined at 500 °C for two hours. As shown in Figure 4, the dilution did result in better separation of the NPs in the salt and the calcination did not result in any particle growth. This stabilization of the NPs in the salt matrix opens new possibilities for post-synthetic processing of NPs and offers an environment that appears ideal for long-term storage of NPs.

Conclusions
Despite the broad applicability of nanomaterials in industry, current methods of NP production are costly and constitute a major hurdle toward wide implementation of NP-based products and technologies. Most NPs are highly stable in their synthesis solution and hence require expensive separation technology, such as the use of membrane centrifugation, for their recovery. We presented a novel NP recovery method via salt recrystallization that has the potential for significant reduction in time and energy required for NP separation. This approach is applicable to both oxide and metal NPs stabilized by ionic and non-ionic interactions. Furthermore, we demonstrated that this approach is highly flexible and can be tailored via the choice of salt for separation of bare NPs, preparation of supported NPs, or even for post-synthetic processing and long-term storage in thermally stable salts. This was achieved without negatively affecting particle sizes and size distributions, further supporting the claim that this salt method constitutes a highly promising candidate for scaling up NP production processes. Moving forward, we plan to determine if thermally treating NPs embedded in a thermally stable salt can be used to induce a change in the chemical structure of a material without resulting in NP growth (e.g. γ - alumina to δ - alumina or reducing NiO to Ni).

Figure 4. TEM images of 2.5 nm Pt NPs from diluted synthesis solution (a) before and (b) after 500°C calcination. NP diameters were (a) (N = 234) 2.2 ± 0.4 and (b) (N = 231) 2.4 ± 0.7 nm. Average diameters and standard deviations were calculated from particle diameters determined from TEM images while using ImageJ.
Acknowledgments
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References


Spike Train Distance Analysis of Neuronal Responses from Prefrontal Cortex

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Abstract

The dorsolateral prefrontal cortex plays a key role in high-order processing and short-term storage of task-relevant information. We apply spike train similarity measures to data recorded from multiple neurons in the prefrontal cortex of a monkey during a working memory task. We compare the efficacy of these methods across a range of parameters to highlight features of the encoding strategy carried out by the monkey during the task. Our findings help to quantify the degree to which information is temporally encoded, while also shedding light on how one might integrate information from populations of neurons to decode certain inputs.

Keywords: Spike train metrics, neural decoding, prefrontal cortex, working memory

Introduction

In order to coordinate complex actions, organisms rely on communication channels throughout the nervous system. This involves lower and higher order processing, where lower order serves the purpose of either directly receiving sensory input like light or sound, or delivering motor output through the contraction or relaxation of muscle fibers. Higher order processing would take signals from the lower order sensory processing, allow the organism to decide what to do with this information, and then carry out that action.

Previous studies have linked the prefrontal cortex (PFC) to high-order processing, as its functionality is vital for adequate performance in tasks where working memory is required or the rules are dynamic \cite{1}. The various regions of the PFC behave differently in working memory tasks, and the dorsolateral prefrontal cortex (DLPFC), which we have chosen to analyze, has been found to encode spatial task-related information through sustained delay activity \cite{2}. Therefore, one should be able to extract spatial details during a task from the activity of individual neurons in the DLPFC.

While it is generally accepted that neurons communicate through their action potentials, or spikes, many groups have focused on studying how the brain reads these spike trains to determine what information each neuron is conveying \cite{3}. Certain neurons appear to exhibit rate coding, where one can decode a stimulus based only on the firing rate of a neuron during a time window \cite{4}. In light of findings that demonstrate that the timing of as few as a single spike can encode a significant portion of the information about a stimulus \cite{5}, naturally many have developed and applied techniques that factor in this temporally encoded information \cite{6,7,8}.

One such method that quantifies the metric distance between spike trains has been applied to neural data from several brain regions with promising success \cite{9}. Others have extended this method for improved functionality, namely for the purpose of analyzing populations of simultaneously recorded neurons \cite{10,11}. Our work applies these methods of spike-train distance to data recorded from the DLPFC, which has not been previously seen in the literature.

Methods

Experimental Setup

In the experimental setup, a macaque monkey sits in front of a screen, with its head fixed. The screen displays a 3 x 3 grid, with the center square containing a fixation cross. Once the monkey has established fixation on the center, as determined by an eye tracker, one of the eight perimeter squares illuminates red
for 300 ms (target). After a 1000 ms delay period, a different perimeter square illuminates green for 300 ms (distractor). Then, after another 1000 ms delay period the fixation cross disappears and the monkey must attempt to make a saccade towards the location of the target square (Figure 1). If the monkey performs the task correctly, it is given a juice reward. Otherwise, there is no juice reward. After an inter-trial interval, a new trial with a separate target-distractor pair is performed. For each trial, neural activity recorded by implanted microelectrode arrays are amplified, digitized, and saved to a computer. The data is then high-pass filtered, and sorted into spike trains using a hidden Markov model algorithm [12].

**Algorithm Overview**

In order to compare the spike trains across the 621 trials, we employ the metric spike train distance algorithm developed by Victor and Purpura [6]. This method, based on the edit-distance algorithm [13], determines the distance between spike trains by finding the total cost, which is a unitless measure of operations performed, to transform one train into another via insertions, deletions, and shifts. Insertions and deletions are assigned a fixed cost of one, each, whereas shift costs are determined by $q|\Delta t|$, where $q$ is a sensitivity parameter with units of seconds$^{-1}$ and $\Delta t$ is the time change associated with the shift. As a consequence of these cost values, two spikes are similar and can be transformed by a shift if $|\Delta t| < 2/q$, because in that case $q|\Delta t|$ would be less than the cost of two, associated with deleting the original spike and inserting it at the new location (Figure 2).

Optimally, given a range of stimuli, one would want to select a $q$ value for which distances between spike trains elicited by the same stimulus are low, while distances to other stimuli are higher in comparison. At this optimal $q$ value, the quantity $2/q$, with units of seconds, characterizes the time scale of the spike train producing neuron. At one extreme, with $q = 0$, the timing of each spike is irrelevant and distances are determined by the difference in the number of spikes between the two spike trains, making it a rate code. With $q \rightarrow \infty$, only spikes that occur at the same instant are considered similar, so the metric becomes a coincidence detector. An optimal $q$ value falling between these two extremes has been used by some as a means of describing the
encoding nature of neurons within a brain region [6,10], but others have called into question the accuracy by which this parameter describes the neural code [14]. This method is applied for all of our single-cell evaluations. Aronov [15] provides an extension to the spike train distance metric by allowing for spike trains from pairs of neurons to be analyzed. A new parameter \( k \) is introduced, which represents the cost of reassigning the label of a spike during a shift, i.e. transforming a spike from one neuron to a spike from a different neuron. Therefore, in this metric, shifts now have a cost of \( q|\Delta t| + k \) when reassigning labels and \( q|\Delta t| \) otherwise. When \( k = 0 \), the spike trains create a population code where the origin of each spike is ignored. When \( k \geq 2 \), the spike trains are interpreted as a labeled line, where the pairwise distance is treated as the sum of the individual distances of each of the two neurons. When \( k \) falls between those two values, the spectrum determines the relative importance of the origin of each spike. In order to determine the optimal \( q \) and \( k \) values for each neuron/pair of neurons, one must find the combination of these values that results in the highest degree of discrimination between stimuli.

For evaluating the discriminative performance of each neuron/pair of neurons across a range of parameters, two methods are used. The first, as used in Victor and Purpura [6] and Aronov et. al [10], separates each spike train into one of eight groups (for eight different target locations) and creates an 8 x 8 confusion matrix with \( N \) (number of trials) entries, where for each spike train from a certain trial (corresponding row), we assign it to one of eight different groups based on which group of spike trains its average distance to is lowest (corresponding column). Therefore, for each range of parameters (\( q, k, \) cells, time window, etc.), we can depict how accurately this analysis technique categorized the spike trains by the degree to which the confusion matrix is diagonal, and we can quantify this by an amount of information, in bits, where 3 bits is maximal because \( \log_2[8 \text{ locations}] = 3 \) bits.

The second method opts for a qualitative rather than a quantitative approach. Drawing from other work in visualizing spike train distances, we produce a low dimensional, graphical representation of higher dimensional data [11]. This is achieved by applying the t-distributed stochastic neighbor embedding (t-SNE) algorithm [16] to matrices containing spike train distances. Using either single-unit or multi-unit spike train distance data, an \( N \)-dimensional matrix of each trial-to-trial distance is inputted into the t-SNE algorithm, which returns a 2-dimensional plot, effectively preserving relative spacing between each trial data point.

Results
Optimizing Parameters
Given the two-parameter nature of the multi-unit metric space analysis approach, first we seek to find general trends in the optimal parameters. Values of \( q \) were chosen from a range found to produce optimal information using the single unit method for the recorded neurons. \( k \) values were varied from 0 to 2. Using intermediate \( k \) values (\( 0 < k < 2 \)) requires the use of more computationally expensive algorithms than the single unit method, which is \( O(N^2) \), where \( N \) is the number of spikes per train. The multi-unit algorithm has a complexity of \( O(N^{d-1}) \), where \( L \) is the number of labels, or neurons per train. This increased complexity for even the bivariate case (two neurons) restricts us to only analyzing pairwise information for 10 of the 58 neurons sampled during the target time window. These 10 neurons were shown to encode spatial information during the target window using other analytic methods.

Figure 3 contains the redundancy index of neuron pairs [17] for the different \( k \) values (at optimal \( q \) value) across four neurons that showed considerably higher degrees of encoding than the other six neurons in this method (although similar results were found with more error when all ten neurons were included). Redundancy index is a measure of the degree to which two neurons encode information jointly. For an index of 0, joint information is completely independent. For a value of 1, information is completely redundant. For values between 0 and 1, information is partially

![Figure 3](image-url)
redundant. And for values greater than 1, information is contradictory. Seeing as redundancy gradually drops for higher k values, and a k value of 2 is preferable due to computational constraints, this value was chosen for subsequent multi-unit analysis.

**Information Across Time Intervals**

We next looked to see how both information in the system and the effectiveness of the method evolved over the duration of the experiment. To do this, we first analyzed all 58 cells and found which ones encoded at least 0.1 bits of information for some 300 ms time window (fixation, target, early delay 1, late delay 1, distractor, early delay 2, late delay 2, saccade) using the single unit method for a wide range of q values. Next, we computed the pairwise information values, with k = 2, for these encoding cells at each time window. Finally, we computed an ensemble information by comparing each of these encoding cells’ spike trains at once, essentially taking an aggregate sum of each cell’s distance matrix and calculated the information from those distances. For comparison, we included the information found using a rate code for both best pairwise and ensemble coding over time, as well as the best single-unit information (Figure 4). The pair of neurons that encode the most pairwise information at each time window changes over time, as shown in Figure 5, where the four different high-information pairs exhibit peaks at different times.

![Figure 4. Information encoded across trial duration. H_pair indicates information found using the multi-unit method with two neurons at optimal parameters. H_single is information from single-unit method. All values are from the maximum single neurons/pairs at each respective time period. H_ensemble is information from multi-unit method with all encoding cells. Rate indicates a q value of 0.](image-url)
t-SNE Visualization

As described in another study [14], the method above of quantifying information is very sensitive to the classifier used, so to construct a better visualization of the clustering performance across different groups of cells, we apply the t-SNE algorithm to constructed trial-to-trial distance matrices (Figure 6). Ideally, as the distances between more neurons are included in the distance matrix through multi-unit analysis, the locations should separate further. The visualization for the best single cell was not included because of uncharacteristic t-SNE output. Additionally, we compare the Aronov method’s results to both a rate code and to a different multivariate application of the Victor distance, which applies the t-SNE algorithm to an $N \times MN$ distance matrix, where $N$ is the number of trials and $M$ is the number of neurons [11].
Discussion
Optimal Parameters
We have applied spike train distance metrics to neural data recorded from the DLPFC, which has a higher sensitivity to individual spike times than other binned methods. To take full advantage of the many cells that we were able to record simultaneously during our experiment, we used multi-unit extensions of the single unit algorithm. For the cells that encoded target location, greater information was obtained through pairwise or ensemble analysis, with the least redundancy when each spike train was considered separately (i.e. the k parameter value of 2).

Information Across Time Intervals
Although for the target period there was a considerable difference in the information encoded using the time sensitive metric over a rate code, for the subsequent time periods this difference essentially vanished. One of the reasons for this could be because one cell, g40c01, encoded a high amount of information (0.4 bits) during the target period and benefitted the most from a higher temporal precision (approximately 8 ms, a level of magnitude lower than the majority of other cells analyzed), therefore making the rate code much less effective in this time window. However, most other cells were not this time-sensitive and for that reason, rate coding performed as well if not better across the rest of the experiment.

t-SNE Visualization
The t-SNE visualizations do indicate that the spike train distance metric lends itself well to our experiment, as in the late delay 1 period, the 8 locations form a circle that resembles the shape of the 3 x 3 grid. It is unclear whether the failure to produce clear clusters is due to the particular method or the fact that only a handful of recorded cells contributed significantly (greater than 0.1 bits above shuffled information) to location discrimination. Previous experiments concerning spatial working memory seem to indicate that more of our cells should have contributed to the information through receptive fields [2].

Conclusions
From our results, spike train similarity measures appear to have strong potential for expanding our understanding of the DLPFC, but that potential largely depends on the metric used. Already, many other multi-unit extensions have been developed [18,19,20] that could be applied in future studies. Although few conclusions can be made about the spike resolution of spatial working memory encoding neurons in the DLPFC, the t-SNE visualizations clearly demonstrate that target location can be decoded using spike train distance metrics. Further research could be focused on analyzing how location encoding performance is affected by variations in experimental setup, such as the inclusion of distractors during the trial sequence.

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References


Biofuel Production through Anaerobic Digestion Effluent Using *Yarrowia lipolytica*

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**Abstract**

Lipid biofuels offer a safe and biodegradable alternative for nonrenewable fossil fuels, especially as greenhouse gas emissions continue to rise and energy demands increase. Yet, there is an emerging need to make them more economically feasible, without diminishing the supply of resources reserved for the human population. Volatile fatty acids (VFAs) obtained from anaerobic digestion effluent are currently being explored as a new and less expensive substrate source, also satisfying the need to valorize wastewater by upgrading the organic compounds high in carbon content into fuel. The potential of *Yarrowia lipolytica* to produce lipid biofuels from anaerobic digestion effluent was investigated by using acetic, propionic, and butyric acid, individually and in synthetic mixtures, as substrates. It was found that *Y. lipolytica* accumulated biomass in the different substrate conditions, with acetic acid having less inhibition on cell growth than the higher carbon chain acids. Consumption of the VFAs by *Y. lipolytica* was also demonstrated. Acetic acid was consumed the fastest, followed by butyric and propionic acid. When discussing biofuel production, it is also important to consider factors such as the pH of the growth medium, because in these experiments, a less acidic pH resulted in enhanced cell growth at concentrations that are normally found to be inhibitory. In summary, it has been demonstrated that *Y. lipolytica* is suitable for different conditions of anaerobic digestion effluent and, therefore, is an adequate microorganism that can be used in linking wastewater to biofuel production.

**Keywords:** Lipid biofuels; *Yarrowia lipolytica*

**Introduction**

Lipid biofuels serve as biodegradable and nontoxic alternatives to petroleum-based diesel as they do not produce sulfur emissions. They also offer a sustainable solution to the rising energy demands as they are created from a continually renewable source, and thus are able to replace the nonrenewable fossil fuels used in car engines and heating systems. However, the sustainability of lipid biofuels is up for question because the use of substrates for biofuel production is diminishing the supply of resources (food, crops, and water) reserved for the human population. Glucose is one substrate that is efficiently converted into value-added products; however, glucose is expensive and the use of glucose has skyrocketed the price of food [1]. Furthermore, the use of land to cultivate oil crops for biofuel production indirectly contributes to increasing food prices. In an attempt to make biofuel production more sustainable and economically feasible, volatile fatty acids (VFAs) obtained from the discharge of anaerobically fermented wastewater are being explored as a substrate source [1]. Using anaerobic digestion effluent is advantageous because it is a means of waste disposal and could potentially yield value-added products concurrently.

Using a biological process, such as a microorganism, is desirable to accomplish conversion of carbon sources into lipid biofuels because it is environmentally friendly and cost-effective. Species like *Yarrowia lipolytica* are candidate organisms because they are oleaginous, meaning they can accumulate 20–65\% of their dry weight in lipids [2]. Greater lipid accumulation is important because it translates to greater biofuel production. *Y. lipolytica* is also versatile in its ability to use different carbon sources as substrates, ranging from ethanol, glycerol, and glucose to organic acids.
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[2]. Different substrates can be converted to lipids of varying composition and amount, which influences its potential to be used as a biofuel.

This research explores the potential for conversion of VFAs into lipids by *Y. lipolytica* under different substrate conditions relevant to anaerobic digestion effluent, which can differ by VFA mixture and concentration according to the source; although, acetic acid is usually the dominant VFA present [3]. Thus, the objectives of this study are: to evaluate the ability of *Y. lipolytica* to use different VFAs, individually or in mixture; to investigate the effects of the acids on cell growth; and to characterize the consumption pattern of the VFAs by *Y. lipolytica*.

**Methods**

*Yarrowia lipolytica*

A strain of *Y. lipolytica* was obtained and revived from storage at -80°C. Cells were routinely cultured on yeast extract, peptone, and D-glucose (YPD) at 30°C. Aseptic technique was followed throughout the experiment.

**Volatile Fatty Acids (VFAs)**

Bulk solution of 100 g/L acetic acid, 20 g/L propionic acid, and 20 g/L butyric acid were made and stored at room temperature. All general chemicals and media components were purchased from Sigma-Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA).

**Analytical Methods**

Cell growth was monitored by measuring OD600 using a UV-visible spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA). Acetic, propionic, and butyric acid were quantified by high performance liquid chromatography (Agilent Technologies 1200 series) equipped with a refractive index detector and a Rezex ROA-Organic Acid H+ (8%) column (Phenomenex Inc., CA). The column was eluted with 0.005 N H2SO4 as the mobile phase under the flow rate of 0.6 mL/min at 50 °C.

**Batch Culturing Experiments**

Each of the solutions discussed below was prepared in a 125 mL Erlenmeyer flask, inoculated with *Y. lipolytica*, and placed on a shaker at 250 rpm at 30°C, with an initial optical density OD0 = 0.5. Optical density was measured at 600 nm using a UV-visible spectrophotometer at 10X dilution for each sample that was taken. Samples were also stored for VFA analysis by HPLC at 5X dilution at -20°C. The experiments were stopped after the stationary growth phase had been reached, i.e., when cell growth plateaued or declined after reaching a maximum value indicating cells were fully grown.

**Experiment 1 (Single VFA fermentation)**

Four 20 mL solutions of yeast extract, peptone, and acetic acid (YPA) at 1, 2, 4, and 6 g/L were prepared. Similar solutions were made for butyric and propionic acid at 1, 2, and 4 g/L. Samples of inoculated medium were taken approximately every 24 h until 72 h after the addition of yeast.

**Experiment 2 (1:1:1 Mixture fermentation)**

Two 20 mL solutions of yeast extract, peptone, and a 1:1:1 mixture of acetic, propionic, and butyric acid at 3 and 6 g/L were prepared. Samples of inoculated medium were taken between every 4-15 h until 41 h after the addition of yeast. Initial pH and pH after fermentation was recorded for all conditions.

**Experiment 3 (Mixed fermentation at ratios mimicking anaerobic digestion effluent and controlled pH)**

Six 20 mL solutions of yeast extract, peptone, and a 1) 4:4:2, 2) 8:1:1, and 3) 6:1:3 mixture of acetic, propionic, and butyric acid at 3 and 6 g/L were prepared. Samples of inoculated medium were taken between every 5-16 h until 52 h after the addition of yeast. Before inoculation occurred, 50-100 µL of buffer was added to ensure an initial pH of 6. Initial pH and pH after fermentation was recorded for all conditions.

**Cell growth and VFA consumption**

For each of the mixture fermentations, the specific growth rate (µ) and the specific VFA consumption rate (sVCR) were calculated using the following equations [1,4]:

\[
\mu = \frac{\ln(O_{D2} / O_{D1})}{\Delta t}
\]

\[
sVCR = \frac{C_{1} - C_{2}}{\Delta t}
\]

where OD, C, and Δt represent the optical density at 600 nm, VFA concentration in g/L, and time elapsed between the samples of interest in h, respectively. The subscripts ‘1’ and ‘2’ represent the samples at time points 1 and 2.
Results
Cell growth and VFA consumption under conditions with single substrate
The cell grew in all three individual VFAs; however, growth was slightly inhibited at 4 g/L acetic acid and substantially inhibited at 4 g/L butyric and propionic acid (Figure 1). Cell growth did not occur at 6 g/L of acetic acid (results not shown). Acetic acid was completely consumed at all concentrations after 24 h; butyric and propionic acid remained at the end of the experiment at 4 g/L, with the concentration of butyric acid increasing at the 72 h time point (Figure 2).

Cell growth and VFA consumption under conditions with mixed substrate
Cell growth in a 1:1:1 mixture of acetic, propionic, and butyric acid over time is shown in Figure 3. At 3 g/L, *Y. lipolytica* grew at a rate of 0.151 h⁻¹ (Table 1), reaching its maximum at 26 h. Growth was inhibited in the 6 g/L solution, growing at a rate of 0.034 h⁻¹ (Table 1). All VFAs were completely consumed in the 3 g/L solution by 14 h, although at different rates (acetic = 0.059, propionic = 0.108, and butyric acid = 0.083 g/g dry cell wt/hr, Table 1). In the 6 g/L solution, the VFAs were not completely consumed. Similar to the findings in Experiment 1, butyric acid and propionic acid reappeared at the end of the experiment.

![Figure 1](image1.png)

**Figure 1.** Cell growth in a) acetic, b) propionic, and c) butyric acid over time (Experiment 1)

![Figure 2](image2.png)

**Figure 2.** Concentration of a) acetic, b) propionic, and c) butyric acid over time (Experiment 1)

![Figure 3](image3.png)

**Figure 3.** Cell growth and concentration changes of VFAs under incubation conditions with a) 3 g/L and b) 6 g/L of a 1:1:1 acetic:propionic:butyric mixture (Experiment 2)
Table 1. Summary of mixture fermentation performances of Y. lipolytica

<table>
<thead>
<tr>
<th>Expt. #</th>
<th>Conc. (g/L)</th>
<th>Mixture</th>
<th>Specific growth rate, µ (h⁻¹)</th>
<th>Acetic acid consumption rate (g/g dry cell wt/hr)</th>
<th>Propionic acid consumption rate (g/g dry cell wt/hr)</th>
<th>Butyric acid consumption rate (g/g dry cell wt/hr)</th>
<th>Initial pH*</th>
<th>pH after ferment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3:1:1:1</td>
<td>0.151</td>
<td>0.059</td>
<td>0.108</td>
<td>0.083</td>
<td>4.5</td>
<td>4.5</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>6:1:1:1</td>
<td>0.034</td>
<td>0.052</td>
<td>0.024</td>
<td>0.047</td>
<td>4.0</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>4:4:2:2</td>
<td>0.269</td>
<td>0.234</td>
<td>0.108</td>
<td>0.048</td>
<td>6.0</td>
<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>8:1:1:1</td>
<td>0.259</td>
<td>0.407</td>
<td>0.033</td>
<td>0.099</td>
<td>6.0</td>
<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>6:1:3:3</td>
<td>0.242</td>
<td>0.210</td>
<td>0.016</td>
<td>0.178</td>
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<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
<td>6</td>
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<td>0.037</td>
<td>0.083</td>
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<td>6.0</td>
<td>9.0</td>
</tr>
<tr>
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<td>0.217</td>
<td>0.010</td>
<td>0.027</td>
<td>6.0</td>
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<tr>
<td></td>
<td>6:1:3:3</td>
<td>0.163</td>
<td>0.085</td>
<td>0.011</td>
<td>0.000</td>
<td>6.0</td>
<td>6.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Figure 4. Cell growth and concentration changes of VFAs under incubation conditions with a) 4:4:2 (3 g/L), b) 4:4:2 (6 g/L), c) 8:1:1 (3 g/L), d) 8:1:1 (6 g/L), e) 6:1:3 (3 g/L), and f) 6:1:3 (6 g/L) acetic:propionic:butyric mixture (Experiment 3).

Cell growth and VFA consumption under conditions with mixed substrate at ratios mimicking anaerobic digestion effluent and controlled pH

Similar levels of cell growth were reached across all substrate conditions, independent of total VFA concentration and mixture (Figure 4). However, in all 3 mixtures, the cell grew at a slightly faster rate in 3 g/L as opposed to 6 g/L (Table 1). At 3 g/L, there was not a significant difference in Y. lipolytica’s growth rate among the three mixtures (range 0.242-0.269 h⁻¹, Table 1); however, there was some variation in the growth rates at 6 g/L. The fastest growth occurred in the 8:1:1 mixture (0.244 h⁻¹, Table 1), while the slowest growth occurred in the 6:1:3 mixture (0.163 h⁻¹, Table 1). Additionally, in five out of the six mixed substrate conditions, acetic acid was determined to be the fastest VFA consumed by Y. lipolytica (Table 1).
Discussion

The first experiment contributes to our understanding of *Y. lipolytica*’s growth and consumption patterns in single acid fermentation. It was observed that *Y. lipolytica* can grow on all three VFAs tested, with 1 and 2 g/L being the most optimal concentrations since the VFA was completely exhausted and cell growth reached its maximum. There was an inhibitory effect on cell growth at 6 g/L acetic acid, consistent with the literature, which reported that above 5 g/L *Y. lipolytica* will exhibit inhibited growth and lipid accumulation [5]. There can be many different reasons for growth inhibition, such as substrate preference, kinetics of substrate conversion reactions, and substrate transport and uptake. Since the 6 g/L solution of acetic acid was confirmed inhibitory, it was excluded from further individual experimentation with propionic and butyric acid.

The second experiment provides us with information about *Y. lipolytica*’s behavior in a 1:1:1 mixture of VFAs. *Y. lipolytica* was able to grow at 3 g/L total VFA, but the 6 g/L solution substantially inhibited growth, possibly due to an acidic initial pH as recorded in Table 1. The pH after fermentation, pH=9 (4.5) for the 3 (6) g/L condition, is added for completion to show that the acids are being used (not being used) because of an increase (no increase) in pH from the initial pH. Based on this hypothesis, the next round of experiments (Experiment 3) was decided to be carried out under less acidic conditions (pH=6).

In order to mimic actual anaerobic digestion effluent, a synthetic mixture of VFAs was created using similar ratios found in real anaerobic digestion effluent. Acetic acid is the most prevalent VFA found in anaerobic digestion effluent [3], so ratios were chosen to have higher proportions of acetic acid. It was determined that *Y. lipolytica* grew faster in mixtures with greater acetic acid content and consumed acetic acid the quickest. Also, the adjustment of pH to a less acidic value (pH=6) eliminated the growth inhibition at 6 g/L seen in Experiment 2.

The trend observed throughout all three experiments was that the 3 g/L solutions provided a more viable growth condition for *Y. lipolytica* compared to 6 g/L. Furthermore, as the number of carbons in the VFA increased, as in the case from acetic to propionic, cell growth and acid consumption decreased, probably because substrates with fewer carbon atoms are easier for *Y. lipolytica* to use and break down. It was also common for the VFAs to reappear by the end of the experiment. These findings suggest further synthesis of the VFAs, possibly due to a metabolic shift as the substrate is depleted; metabolic pathways not yet understood may reverse and reproduce the VFA. These results can be used to predict how *Y. lipolytica* can grow in real world situations. If the composition of an acid mixture from a wastewater treatment plant is known, these results can be used as guidance for design strategies, such as adjusting the pH, to synthesize lipids in the most optimal manner.

Limitations and Future Considerations

The accumulated lipids of the grown cell in different substrate conditions were not able to be characterized nor quantified due to limited timeframe and lack of accessibility to a working gas chromatograph mass spectrometer (GC-MS). Cell growth was the only indicator used to estimate lipid accumulation, with the assumption that lipid quantity was proportional to biomass of the yeast cell. Direct quantification of lipid is necessary to determine the actual production capability of lipid from VFAs. Additionally, it is important to characterize composition of lipid produced, which influences the potential to be used as biofuel. One study reported that the lipids synthesized by *Cryptococcus albidus* contained 70% unsaturated fats, which is similar to the commercial feedstock used for biodiesel production [1]. Thus, future experiments under conditions of interest will include analysis by GC-MS to determine the degree of lipid accumulation and composition.

The data reported here do not represent biological replicates as none of the experiments were repeated due to limited experimental conditions; therefore, it has not been demonstrated that these results are replicable. However, the literature shows that similar experiments can be highly replicable [5] so future experiments under conditions of interest will be done in triplicate. This will allow for statistical tests to be performed in order to assess significant differences among growth rates and VFA consumption rates.

Future work is also needed to characterize *Y. lipolytica*’s behavior in real anaerobic digestion effluent. This study’s use of a synthetic mixture to mimic anaerobic
digestion effluent does not fully demonstrate that *Y. lipolytica*’s microbial power will translate from lab bench to real-world applications.

**Conclusions**

It was found that *Y. lipolytica* accumulated biomass in the different substrate conditions relevant to anaerobic digestion effluent. Among the three different acids tested, acetic acid had less inhibitory effect on cell growth than the higher carbon chain acids. Furthermore, consumption of the organic acids by *Y. lipolytica* was demonstrated. However; the consumption rates varied for the different acids tested, with acetic acid being consumed the fastest, followed by butyric and then propionic acid. Also, when discussing biofuel production, it is important to consider factors such as the pH of the growth medium, because in these experiments, a less acidic pH resulted in enhanced cell growth at concentrations that are normally found to be inhibitory. In summary, it has been demonstrated that *Y. lipolytica* is suitable for different conditions of anaerobic digestion effluent, and therefore, is an adequate microorganism that can be used in linking wastewater to biofuel production, allowing for a more sustainable approach to replace using glucose and other agricultural resources.

**Acknowledgments**

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**References**


Influence of Sputter Power and Wafer Plasma Cleaning on Stress and Phase Formation of As-Deposited Tantalum Thin Films

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Abstract
Tantalum (Ta) thin films are used in a variety of applications including, but not limited to, microelectronics. Strength, reliability, and corrosion resistance at high temperatures are all important factors that make Ta a valuable material to study. Ta thin films can take the form of either a stable bcc α phase (also bulk Ta phase) or a metastable tetragonal β phase. The phase formation in as-deposited thin films, phase transformation from β-Ta to α-Ta, and the resultant stresses from deposition and transition have been studied for decades but are still not entirely understood. However, a better understanding of how stresses develop and how phases form during the processing of thin films is essential for designing new components with new properties or dimensions.

Specifically, changing processing parameters, such as the sputter power used during sputter deposition, will change the microstructures that develop within the film. In this present study, these processing parameters were investigated by sputtering a series of thin films, adjusting sputter power and wafer plasma cleaning parameters, and observing the resulting stresses and phases present. The thin films were then characterized using x-ray diffraction, thickness measurements, resistivity measurements, and substrate curvature measurements. These results were then compiled in attempt to draw conclusions about the influence of processing parameters on stress and phase formation.

Keywords: mechanical properties

Abbreviations: XRD – x-ray diffraction

Introduction
Ta thin films have been studied for decades [1-5]. Findings indicate two phases are present in Ta, a stable bcc phase and a metastable tetragonal phase [1]. Each phase has distinct properties including, but not limited to, resistivity, and accordingly a certain phase is often specific to a certain application. β-tantalum has been used in tantalum thin film capacitors [6] while α-tantalum is the “preferred phase” for diffusion barriers between copper and silicon in microelectronic devices [1].

The presence of these phases and the stresses in the films are dependent on a large number of processing parameters and environmental conditions, including but not limited to the following: cleanliness of the system [6], sputter pressure [2, 5, 7], sputter power [4, 5, 7], type of substrate [4], RF substrate bias voltage [2, 4], impurities [1, 4, 6, 7], and temperature [2, 6]. The phase transformation temperature has been determined to be somewhere between 600 and 800 °C [2] but also well below 600 °C [1], mostly depending on the impurities of the Ta thin film introduced during deposition or during heat treatment. Overall, findings tend to be inconsistent [6], and it is difficult to draw overarching conclusions as the cleanliness of the systems, achievable base pressures, and measurement techniques vary from study to study.

The processing parameters used during sputter deposition influence the microstructure and phases that form in the thin films. Different phases have different material properties, including resistivity, which is significant for various applications. Since the ability to predict how stresses will develop in new designs is valuable in predicting failure in thin film parts, one of the two objectives of this study is to better understand the development of stresses in as-deposited tantalum thin films. The second objective we focus on is the effect of sputter power and wafer plasma cleaning on the as-deposited Ta phase.
Experimental Methods

Silicon wafers 76.2 mm in diameter (Silicon Valley Microelectronics Inc.) were individually removed directly from their double wrapped boxes and prepared. First, they were inspected for dust particles and ultra-high purity helium (Matheson Gas) was sprayed onto the surface to remove any visible particles. There was no additional “cleaning” step performed, since past results showed that the use of isopropanol and acetone results in less clean surfaces. Next, the wafer was mounted onto the substrate holder, which has been modified so that there is sufficient space for the wafer to buckle or bend as a result of stress.

The substrate holder with the wafer was then placed into a load lock which was pumped down to less than 3.0x10^-6 Torr, by a turbo pump (Pfeiffer Vacuum) assisted by a roughing pump. Once the pressure had reached the atomic regime, the wafer was transferred to the main chamber where deposition took place. The wafer was positioned at the top of the chamber, facing down toward the target guns. This chamber was pumped down using a getter pump (SAES) and a cryogenic pump (Oxford Instruments Austin) to less than 2.0x10^-8 Torr, following a main chamber bakeout at temperatures around 90–100 °C for an hour and a getter pump heating procedure.

The thin films were deposited with an AJA International Inc. ATC Orion Sputtering System using a Ta target of 50.8 mm in diameter (99.95% purity, Lesker). Some of the substrates were sputter cleaned prior to deposition at 25 W for varying times and pressures. Following that step, the target plasma was struck at 35 W and left running for five minutes with a closed target shutter to remove any contaminants or oxides from the target itself and ensure a steady uniform deposition rate prior to actual deposition. The power to the target was then ramped up to the desired sputtering power and the target shutter was opened. Deposition took place over a course of 16 minutes at 8 mTorr. The processing gas used was ultra-high purity argon (Matheson Gas), at a flow rate of 16–20 standard cubic centimeters per minute (details, see Table 1).

The stresses of the thin films during deposition were measured using a kSA MOS curvature measurement system with the curvature of the bare substrate before deposition as reference. In this system, a laser array is projected from below onto the substrate’s surface and reflected back. The reflected array of dots changes position and spacing as the curvature of the substrate changes. The calculated curvature difference was computed into a stress thickness product, which was then converted to stress with the film thickness.

The thicknesses of the films were measured using a mechanical Alpha-Step IQ Profiler in the Nanoscale Fabrication and Characterization Facility. The step size was measured by dragging the tip from a region of uncoated, but sometimes shadowed, substrate to a coated region about 2 mm closer to the center of the substrate. Multiple values were taken and these numbers were averaged, yielding only an approximate thickness due to some additional curvature found in the coating that could not be accounted for in step size measurement.

In order to estimate the portion of each phase present, film resistivity was measured using a four point probe (Jandel, Model RM2) connected to a Keithley 2001 Multimeter for a more accurate display. The current was set to 100 μA and potential differences were measured at five positions on the wafer. For microstructural analysis, XRD was performed using a PANalytical Empyrean with a cobalt Kα radiation source. Patterns were recorded from 2θ=20° to 80° with a step size of 0.02° and no tilt.

Table 1. Deposition parameters of Ta samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sputtering Power [W]</th>
<th>Sputtering Duration [min]</th>
<th>Sputter Cleaning Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>125-1</td>
<td>125</td>
<td>16</td>
<td>Not cleaned</td>
</tr>
<tr>
<td>200-1</td>
<td>200</td>
<td>16</td>
<td>Not cleaned</td>
</tr>
<tr>
<td>200-2</td>
<td>200</td>
<td>16</td>
<td>20 mTorr, 5 min</td>
</tr>
<tr>
<td>200-3</td>
<td>200</td>
<td>16</td>
<td>26 mTorr, 1.5 min</td>
</tr>
<tr>
<td>200-4</td>
<td>200</td>
<td>16</td>
<td>8 mTorr, 1.5 min</td>
</tr>
<tr>
<td>75-1</td>
<td>75</td>
<td>16</td>
<td>8 mTorr, 1.5 min</td>
</tr>
</tbody>
</table>
Results

Figure 1 displays the stress-time results for the films with retrievable data. Excluded are samples that incurred issues with laser array positioning or with saving. Using the average thickness from each film sputtered at a specific power, an average growth rate was calculated. This unique growth rate (i.e., approximately 1.8 Å/sec for 200 W and 0.4 Å/sec for 75 W) was then used to compute the stress of the film at a given time. It can be seen that films with a given sputtering power approach similar values of stress, with the final stress increasing with sputter power.

Table 2 below displays the results for the average potential differences, resistances, and thicknesses for several of the films.

Table 2. The films and their approximate resistivities

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Voltage [mV]</th>
<th>Resistance [Ω]</th>
<th>Thickness [nm]</th>
<th>Resistivity [µΩ·cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>125-1</td>
<td>0.4279</td>
<td>19.4</td>
<td>95</td>
<td>185</td>
</tr>
<tr>
<td>200-1</td>
<td>0.2465</td>
<td>11.2</td>
<td>165</td>
<td>184</td>
</tr>
<tr>
<td>200-2</td>
<td>0.2354</td>
<td>10.7</td>
<td>230</td>
<td>245</td>
</tr>
<tr>
<td>200-3</td>
<td>0.2747</td>
<td>12.4</td>
<td>165</td>
<td>205</td>
</tr>
<tr>
<td>200-4</td>
<td>0.2701</td>
<td>12.2</td>
<td>180</td>
<td>220</td>
</tr>
</tbody>
</table>

The resistivities of these films were then calculated using the sheet resistance formula for thin films: \( R_s = \frac{4.53 \times V}{I} \), where V is the average measured potential difference and I is the current sent through the probe [8]. These values of resistance were then multiplied by the films’ respective thicknesses to obtain resistivities.

XRD also was used for phase identification. The XRD patterns displayed peaks that agreed with shifted stick patterns for β-Ta. The peaks that agree with β-Ta are at 2θ=39.4°, which overlaps with a Si substrate peak, and 2θ=44.7° (see Figure 2 below). Unseen are any significant peaks that agree with α-Ta (i.e. 2θ=43.1° or 50.1°). Unlabeled peaks are attributed to the bare wafer.

Figure 1. The approximate stresses found in the films sputtered at different powers and cleaned at different pressures for the first 1000 seconds of deposition.

![Figure 1](image1.png)

Figure 2. XRD results from 200-1 (sputtered at 200 W without wafer cleaning), which is typical of all Ta samples.

![Figure 2](image2.png)
Discussion
Figure 1 shows the stress-deposition time development. There may be no coincidence that sample 75-1 appears to start at extremely positive stresses and then results in the least positive stresses below those sputtered at 200 W, once the stresses steadied out, around 360 seconds. It is found in literature that films that have undergone a phase transformation between beta and alpha see lower tensile stresses, as the films are more relaxed and the stresses are relieved in this more stable and less energetically demanding configuration [2]. Here, we do not assume that a phase transformation took place during the deposition itself, but that the deposition physics play a large role in the as-deposited stress of the thin film.

From the calculated resistivities, the present phases of the as-deposited films can be further determined. \(\alpha\)-Ta is relatively ductile and has an expected resistivity of 15–16 \(\mu\Omega\cdot\text{cm}\). \(\beta\)-Ta is more brittle, has more defects, and thus has a higher resistivity of 170–210 \(\mu\Omega\cdot\text{cm}\) [3]. These resistivity measurements indicate that the as-deposited samples are at least majorly, if not completely, \(\beta\)-Ta. This also is seen in the XRD patterns that correspond to a few peaks of \(\beta\)-Ta and none that significantly agree with \(\alpha\)-Ta. These results continue to agree with the stresses found during deposition using the kSA MOS curvature measurement system. Overall, it appears that films deposited at higher powers yielded films with higher tensile stresses, which also had generally higher resistivities. All of this hints at a higher proportion of \(\beta\)-Ta.

From the characterization methods used herein, there was no clear effect of wafer plasma cleaning and further testing is required to determine the ideal sputter cleaning parameters. This testing would include varying the cleaning duration and power more intensely, and seeing how or if it affects the phases present. Additionally, the effect of cleaning could be better detected using a slower XRD scan and observing a substantial decrease in silicon dioxide identifiable peaks with more intense cleaning. It is important to note that samples 125-1 and 200-1, the two samples that did not undergo sputter cleaning, had the lowest resistivities, which may indicate an influence of sputter cleaning, although further testing is still required, especially because there is no observable trend out of those that were sputter cleaned. There is also a chance that the duration used here for sputter cleaning was too brief to cause any real difference. Additionally, further analysis is required to determine the potential proportions of phases present within the material. Thus, further testing includes determining the ideal sputter cleaning conditions, depositing more films with a more systematic plan, and subjecting the thin films to higher temperatures to observe stress evolution and eventually a phase change.

Conclusions
As seen in literature, Ta thin films undergo a phase transformation from beta to alpha under unique conditions. The existence of phases in the as-deposited wafers can be attributed to a number of processing parameters including, but not limited to, base pressure of the system, temperature at the surface, and substrate conditions. With the great number of processing parameters, it is essential to continue to examine how each of these affects the development of these phases, as the phases present and phase transformation has a large impact on the material’s properties. The results herein indicated that the sputter power and wafer cleaning impact the stresses in the as-deposited thin films, but, at least in the processing parameter range of this study, do not impact the as-deposited phases. Future work is necessary in order to completely analyze the current films, and properly assess the effect of sputter power and wafer plasma cleaning on stress and phase formation of as-deposited tantalum thin films.

Acknowledgments
I would like to thank Dr. Chmielus and members of his lab, including Victoria Mbakwe. This research would not be possible without joint funding by Dr. Markus Chmielus, the Swanson School of Engineering, and the Office of the Provost.
References


Appendix

The results from XRD of a bare silicon wafer prior to deposition is included below for comparison to the coated wafer (see Figure 3 below).

The peak that appears slightly below 2θ=25° in Figure 2 was not seen in the original scan of the bare wafer. However, this peak also appeared in chromium samples, leading us to presume that this peak cannot be attributed to a Ta phase.

Figure 3. XRD results from a bare Si wafer.
Ridge Matching Based on Maximal Correlation in Transform Space

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Abstract
Image matching, a common technique in Computer Vision to identify objects, persons, locations, etc., is widely used in both military and civilian applications. For common image matching algorithms, results may vary when the raw images are captured under different lighting conditions. To reduce the unwanted influence from ambient lighting, we propose a novel method to match images that contain ridge features. The new method uses an established ridge detection algorithm to reduce raw images to sets of ridge points, each point defined by its orientation and location. To perform ridge matching, we find the pair-wise transform between every ridge point from one image and every ridge point from another. The result is a point cloud in transform space. The correlation between two sets of ridge point is equivalent to the density of the point cloud, computed by convolving the point cloud with a blurring kernel. The best match is found as the location in transform space at which the correlation reaches global maximum. We tested the new method on two image pairs; the first image pair contained artificial ridge features and the second pair was sampled from a high resolution image of the human palm. Both tests returned accurate results.

Keywords: Image Matching, Ambient Lighting, Ridge Point, Transform Space

Introduction
The Ambient Lighting Problem
Image-based positioning systems are used for advanced medical imaging techniques. When a set of 2D images—such as acquired by a conventional ultrasound scanner—is used to construct a 3D volume of a structure inside the human body, we require the continual position of the scanner relative to the patient. With an a priori 3D image map of the exterior surface of the patient reconstructed from multiple high resolution images, subsequent images from a small mobile camera can be matched with a correct projection rendered from the 3D map to compute the position of the camera relative to the patient. When the small mobile camera is mounted on the ultrasound scanner, the relative position of the scanner thus determined can be used to construct a 3D volume [1]. A significant problem with this camera-based approach is that images are affected by ambient lighting conditions. The performance of common image matching algorithms is penalized when variations in ambient lighting affects the intensity of image pixels, causing the local features used in matching to become unstable.

Motivation for Ridge Matching
The ridges on the skin are inherent physical structures, often represented by connected groups of salient ridge points within an image. Under normal lighting conditions, these features are resistant to changes in light source location, light source intensity, and shadow patterns. Another key advantage of ridge features is their inherent orientation property. Every ridge point has a well-defined ridge direction, tangent to the ridgeline at the given ridge point. The ridge direction provides additional constraints for computing the rotation between different images. Since ridge features are common on the surface of the human body, the same ridge structure is likely to be detected in images that have significant overlap. By using ridge features, a fast and closed form solution can be reached for matching two camera images with a rigid transform [3] [4].

Methods
Representation of Ridge Features
Our new method first extracts the location of ridge points in the images, using preprocessing algorithm based on an established scale-invariant ridge detection method [2]. The algorithm takes a raw grayscale image I as the input and returns a black and white image BW
as the output. A pixel at the image location \((x, y)\) is considered a ridge point if \(BW(x, y) = 1\).

Each ridge point has an inherent orientation, which is the local direction along the ridge line. To compute the orientation at the ridge point \((x_0, y_0)\), we consider the local Hessian matrix \(H(x_0, y_0)\). Since \(H(x_0, y_0)\) is a symmetric real valued matrix, we may perform eigenvalue decomposition on \(H(x_0, y_0)\) to obtain an orthonormal set of eigenvectors (Eq. 1).

Without loss of generality, let \(|\lambda_1| < |\lambda_2|\). Then the unit eigenvector corresponding to \(\lambda_1\) represents the principle direction of least curvature. The reason to find this eigenvector is that, in a ridge-like structure, the principle direction of least curvature points along the ridge line. From Eq. 1, the eigenvector that corresponds to \(\lambda_1\) is the unit vector \([\cos \theta_0 \sin \theta_0]T\), which can be described by a scalar angle \(\theta_0\) that ranges from \(-180^\circ\) to \(180^\circ\).

The orientation of the ridge point at \((x_0, y_0)\) is therefore mathematically defined as the scalar angle \(\theta_0\), for which \(H(x_0, y_0) [\cos \theta_0 \sin \theta_0]T = \lambda_1 [\cos \theta_0 \sin \theta_0]T\).

The original image \(I\) is reduced to a set of ridge points, represented by a matrix \(S\) defined in Eq. 2.

Each row of \(S\) contains the necessary parameters to describe a ridge point: the ridge point location \((x_i, y_i)\) in the image, and the ridge point orientation \(\theta_i\). The subscript \(n\) in Eq. 2 represents the total number of ridge points found in the original image, and the value is \(n\) is typically less than 5% of the total number of pixels in \(I\). The resulting matrix \(S\) is used as input to a ridge matching algorithm, described next.

**Operations in Transform Space**

To match two images \(I_1, I_2\) with a rigid transform, we need to find the best overall translation and rotation between the two images.

We define the Transform Space \(K\) as the set of all possible rigid transforms \(\{\Delta x, \Delta y, \Delta \theta\}\) between the two images; the best match is represented by a location in \(K\). Since the images have been reduced to two ridge feature matrices \(S_1\) and \(S_2\), each pair of ridge points, \(v_1 = (x_1, y_1, \theta_1) \in S_1, v_2 = (x_2, y_2, \theta_2) \in S_2\), are correlated by a rigid transform \(t: S_1 \times S_2 \rightarrow K\) given by (See Eq. 3 above)

As a consequence of Eq. 3, if \(I_1\) and \(I_2\) have their top and left boundaries aligned (allowing for different sized images with their origins in the upper left corner), by applying the rigid transform \(t\) to image \(I_1\), the locations and orientations of \(v_1\) and \(v_2\) will coincide.

To find the best rigid transform between \(I_1\) and \(I_2\), we map every pair of ridge points \(v_j = (x_j, y_j, \theta_j) \in S_1, v_j = (x_j, y_j, \theta_j) \in S_2\) to a vector in the Transform Space, and the result is a cloud of points in Transform Space \(K\). Every point in the resulting point cloud represents a potential transform mapped from a unique pair of ridge points. When a large number of ridge point pairs map to the same transform, that particular transform is more likely to be correct. In an intuitive interpretation, if the best rigid transform is applied to \(I_1\), the highest number of ridge points will approximately coincide.
Maximal Correlation

In practice, no two ridge point pairs will map to the exact same transform when the images acquired with noise and distortion are sampled at a finite resolution. However, when a good match exists between two images, the point cloud tends to form a dense cluster near an optimum location in the Transform Space \( K \). A measurement of point cloud density at every location in \( K \) provides us the correlation between \( S_1 \) and \( S_2 \) for every possible rigid transform. To do so we define a density function \( D: K \rightarrow R \), where

\[
D(\Delta x, \Delta y, \Delta \theta) = \sum_{v_i \in S_1} \sum_{v_j \in S_2} \delta(\Delta x - \Delta x(v_i, v_j)) \delta(\Delta y - y(v_i, v_j)) \delta(\Delta \theta - \theta(v_i, v_j)) \ast f(\Delta x, \Delta y, \Delta \theta)
\]  

(4)

Results

Test on Artificial Ridge Features

We first tested our method on artificially constructed ridge features. Figure 1 shows a large image containing these artificial features. Every ridge point in this particular set has only four possible orientations: \( \theta = -45^\circ, 0^\circ, 45^\circ, \) or \( 90^\circ \). The location and orientation of every ridge point are precisely known and serve as ground truth for validating our ridge matching algorithm.

Two small patches (See Figure 2) were selected from the large artificial ridge map to simulate the binary images \( BW_1, BW_2 \) after ridge extraction. The offsets were \( (0, 0) \) and the rotation between them was \( 50^\circ \). The patches were used to generate the point cloud in Figure 3. The density of the point cloud was calculated and displayed separately in Figure 4 and Figure 5. The optimal transform was found as \( (0, 1, 50^\circ) \), accurate to a single pixel.

Test on Real Sampled Images

The ridge matching algorithm is next tested on real images of the human palm. Two patches (See Figure 6) were sampled from a larger palm image of the palm. The offset between the sampled patches was \( (80, -20) \) and the rotation between the patches was \( 80^\circ \). Figure 7 shows the binary images produced by the ridge detection algorithm. Figure 8 shows the point cloud generated from the ridge feature matrices. Figure 9 and Figure 10 display the density map of the point cloud in Figure 8. The maximal correlation density

![Figure 1. Image containing artificial ridge features](image1.png)

![Figure 2. Binary images selected from the large artificial ridge map](image2.png)
Figure 3. Point cloud in Transform Space generated from two sets of artificial ridge features

Figure 4. Projection of the density function onto the $\Delta \theta$ axis

Figure 5. Cross section of the density function at $\Delta \theta = 50^\circ$

Figure 6. Sampled images of the human palm

Figure 7. Binary images containing ridge points detected in the palm images

Figure 8. Point cloud generated from real ridge sets
occurs at (80, -19, 80°), also accurate to a single pixel, reasonable given sampling error.

**Discussion**
The artificial ridge features produced strong outlier clusters in the Transform Space. This effect can be attributed to how the artificial ridges were constructed, where all ridge points were forced to take one out of four possible orientations and all ridge lines are long continuous straight lines. There is a risk that when the images being matched contain a large number of repetitive ridge features, the correct match will reliably result from our method. However, in our particular experimental case, the artificial ridge test demonstrated that our method is capable for matching images to within a single pixel of error, warranting further test on real image datasets.

The real palm images produced equally accurate results. The point cloud, compared to that generated from artificial features, is more scattered in Transform Space, but the global peak in the density function is also more prominent for real image datasets.

**Conclusion**
The strong response demonstrated to inherent ridge features allows operations without specialized markers on the skin. As the ridge feature possess inherent orientations, these features are likely to stay stable under normal variations in ambient lighting. Given the present challenge of matching two 2D images with a ridge transform, a process with 3 degrees of freedom (2 translations and 1 rotation), the fact that the individual ridge features also have the same equivalent 3 parameters (2 locations and 1 orientation) results in a closed form solution that is both fast and reliable. The accuracy of the matching algorithm requires that the images being matched contain ridge-like features. By modifying the preprocessing algorithm to detect other types of features such as edges or elliptical blobs, our proposed method can also be generalized to other types of feature matching. We are also working to include additional degrees of freedom, such as scale changes between two images, which can be accommodated by using higher dimensional votes in transform space than simple points.

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**References**

**Figure 9.** Projection of the density function onto the $\Delta \theta$ axis

**Figure 10.** Cross section of the density function at $\Delta \theta = 50^\circ$
Screening a Variety of Catalytic Lewis Pair Moieties for their Hydrogen and Carbon Dioxide Binding Energies

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Abstract
Efficient conversion of CO₂ from various emission sources into valuable chemicals has the potential to reduce net CO₂ emissions from fossil fuels usage. Lewis pairs functionalized in porous materials, such as metal organic frameworks, for CO₂ hydrogenation is a promising method of accomplishing this. Here, we search for Lewis pairs that can bind H₂ stronger than CO₂ by screening H₂ and CO₂ binding energies on various Lewis pairs using the Gaussian 09 software suite. We found that the stronger the electron withdrawing group (F < Cl < Br < CN < CF₃ < NO₂), the stronger both H₂ and CO₂ will bind. The weaker the electron donating group (benzene ≈ CH₃ < OCH₃ < OH < NH₂), the stronger H₂ and CO₂ will bind. We also found that reducing the distance between the Lewis acid-base sites decreases (weakens) the CO₂ binding energies due to steric hindrance. Combining this fact and the trends mentioned earlier, we are able to identify promising Lewis pair catalysts that will bind H₂ more strongly than CO₂ without potentially poisoning the Lewis acid-base site from CO₂.

Keywords: Lewis pairs, CO₂ Reduction, Computational screening, Density functional theory

Abbreviations: Lewis pair (LP), metallic organic framework (MOF), electron donating group (EDG), electron withdrawing group (EWG), density functional theory (DFT)

Introduction
The global growth in the demand for energy means that fossil fuels will continue to be used for the next several decades and that CO₂ will continue to be released into the atmosphere faster than it can be recycled by the natural carbon cycle. CO₂ is considered to be the major greenhouse gas generated from fossil fuels usage. Therefore, CO₂ capture and conversion is a promising way to reduce CO₂ emissions [1]. The reduction of CO₂ into valuable and useable chemicals like formic acid is energetically intensive due to the high thermal stability of CO₂. One way to reduce the required energy is to catalytically hydrogenate CO₂ to formic acid (HCOOH) by activation of CO₂ using homogeneous organometallic catalysts [2]. However, industrial processes typically require heterogeneous catalysts. Ye and Johnson used density functional theory (DFT) calculations to design a heterogeneous catalyst by functionalizing a microporous metal organic framework (MOF) with moieties having both Lewis acid and Lewis base sites (Lewis pairs) [3][4]. These Lewis pairs can heterolytically dissociate H₂ into a proton and a hydride, which react with CO₂ to form HCOOH. However, these Lewis pair functional groups bind CO₂ more strongly than H₂ so that CO₂ poisons the catalyst. Therefore, there is a need to identify new catalytic moieties that bind H₂ more strongly than CO₂ in order to design a catalyst that could be used in practice. Previous work demonstrated that the trends in binding energies on the gas phase moieties (i.e., the Lewis pairs without the MOF) correlate extremely well with binding energies computed for the functional groups bound within the MOFs [4]. This provides an efficient way to screen different functional groups by performing DFT calculations on the gas phase moieties, thus avoiding the computational expense of including the full MOF (which speed up the calculations by a factor of at least 1000). The hypothesis of this work is that the binding energies of H₂ and CO₂ on various Lewis pair functional groups can be modulated by attaching electron withdrawing or electron donating groups to the acid sites of the Lewis pairs. Based on a Sabatier analysis [4], we have identified a target region for H₂ binding energies of 0.0 eV to -0.6 eV, while the target region for CO₂ binding energies is 0.0 eV to 0.3 eV. These ranges allow for favorable binding of H₂ while avoiding poisoning of the sites by strongly bound CO₂.
Methods

Various intramolecular catalytic Lewis pairs (LP) were built using Avogadro molecule editor and visualizer software. Each catalytic Lewis pair consisted of a Lewis base site, either phosphorus or nitrogen, and a Lewis acid site, boron. The skeletal structures of sample intramolecular Lewis pairs are show in Scheme 1. Compound 1 was based on a previously synthesized frustrated Lewis pair 1-[bis(pentafluorophenyl)boryl]-3,5-di-tert-butyl-1H-pyrazole [5]. These so-called frustrated Lewis pairs are molecules designed to have steric hindrance to prevent mutual quenching of the Lewis acid and base sites in solution. Because the functional groups in this study are designed to be covalently bound to the inside of a MOF, they do not require steric hindrance to prevent quenching. Thus, the large phenyl and pentafluoro groups were removed to make 1. 2 was based on a frustrated Lewis pair synthesized by Kehr et al. and like 1, the large substituent groups were removed. Kehr et al. calculated binding energies for hydrogen, so it was important to see if these Lewis pairs could bind CO2 well [6]. 3 was built based on results from 1 and 2 which will be discussed later. We then varied the R groups with various electron donating (CH₃, OH, NH₂, O-CH₃, benzene, t-Bu) and electron withdrawing groups (H, F, Cl, Br, CN, CF₃, NO₂, C₆F₅) using combinatorial techniques to modify the acidity and sometimes, basicity of the Lewis pairs.

To calculate the H₂ binding energy, we added one hydrogen atom to the Lewis acid site and another hydrogen atom to the Lewis base site. Similarly, to calculate the CO₂ binding energy, we attached the carbon to the Lewis base site and attached one oxygen to the Lewis acid site.

Once molecules were built, we exported the Cartesian coordinates from Avogadro and performed DFT calculations to determine the heats of reaction and binding energies of H₂ and CO₂ using the Gaussian 09 software package. We used the M062X density functional with the 6-311g basis set for all the calculations.

We used the Molden software to visualize the optimized structure by measuring the bond length and angles to check if the final structure had physically reasonable bond lengths and angles.

The output file from Gaussian returned the total energy (E), the zero point corrected energy and the Gibbs free energy for each system; in this work we only consider the total energy. The H₂ or CO₂ binding energies on each Lewis pair were defined as

\[ \Delta E = E(\text{M/LP}) - E(\text{LP}) - E(\text{M}) \] (1)

where M represents H₂ or CO₂ and LP represent the Lewis pair.

Scheme 1. Three families of Lewis pairs considered in this work.
Results

The proposed reaction pathway for the binding of H\textsubscript{2} and CO\textsubscript{2} is shown below in Scheme 2.

The most insightful attribute to 1 is that the positions of the substituents, R\textsubscript{1} and R\textsubscript{2} are nonequivalent. Therefore, to show the difference in binding energies for when R\textsubscript{1} was the electron donating group and R\textsubscript{2} was the electron withdrawing group and vice versa, the following equation was made to show the absolute difference in binding energies for the different positions:

\[
\Delta \Delta E = \Delta E(R_{2}, R_{1}) - \Delta E(R_{1}, R_{2})
\]  

(2)

where the first variable represents the substituent R\textsubscript{1} in 1 and the second variable represents the substituent R\textsubscript{2} in 1. Using CH\textsubscript{3} as R\textsubscript{1}, this finding is shown below in Figure 1.

For 2, it was found that decreasing the distance between the Lewis acid and base site reduces the potential for CO\textsubscript{2} to bind well. Figure 2 below shows the substituents and a ratio between H\textsubscript{2} and CO\textsubscript{2} while the cases where H\textsubscript{2} was unbound were eliminated because they are not desirable in practical application. The absolute value of these ratios was taken for clarity.

The general results for 3 are given below in Figure 3, where the majority of the substituents studied are ordered by decreasing electron donating strength to increasing electron withdrawing strength.

The results of H\textsubscript{2} and CO\textsubscript{2} binding energies for specific families of Lewis pairs are shown in Figure 4. 1 with CH\textsubscript{3} as R\textsubscript{1} is in blue, 2 with CH\textsubscript{3} as R\textsubscript{1} and R\textsubscript{2} is in red, and 3 with R\textsubscript{1}=R\textsubscript{2} is in green. The other R groups and families of Lewis pairs are not shown for clarity, but the graph shows the trends for the most promising skeletal structures when changing the unidentified R groups. In the yellow box is the target region for H\textsubscript{2} and CO\textsubscript{2} binding energies (0.0 > H\textsubscript{2} binding ≥ -0.6; 0.0 < CO\textsubscript{2} binding ≤ 0.3 in eV)

**Scheme 2.** The proposed pathway of heterolytic dissociation of hydrogen and its binding to the Lewis pair and CO\textsubscript{2} hydrogenation.
Figure 1. Plot showing the difference of binding energies based on positions of R1 and R2 on 1.

Figure 2. Plot showing ratio between H2 binding and CO2 binding energies. The potentially promising Lewis pairs would have a value less than 1.

Figure 3. Plot displaying trend between electron donating and withdrawing groups and H2 and CO2 binding energies.
Discussion

We calculated $\text{H}_2$ and $\text{CO}_2$ binding energies and found that there seems to be a general trend between the electron donating and electron withdrawing groups on the acid site. The stronger the electron withdrawing groups ($\text{F} < \text{Cl} < \text{Br} < \text{CN} < \text{CF}_3 < \text{NO}_2$), the stronger both $\text{H}_2$ and $\text{CO}_2$ will bind and their energies will be lower. Conversely, the weaker the electron donating group ($\text{benzene} \approx \text{CH}_3 < \text{OCH}_3 < \text{OH} < \text{NH}_2$), the more likely the molecule will bind $\text{H}_2$ and $\text{CO}_2$, but the trend is not as clear as the one mentioned earlier. This is understandable because the increase in strength of electron withdrawing groups makes the acid site less nucleophilic and more electrophilic, while the increase in strength of electron donating groups make the acid site more nucleophilic and less electrophilic. Therefore, the electron withdrawing groups have a higher potential to dissociate $\text{H}_2$ into a hydride ion and have the hydride ion bind to the acid site. Similarly, the more electrophilic acid site with electron withdrawing groups will more easily bind to an electronegative oxygen in $\text{CO}_2$.

The trends discussed above can be used to help modify the Lewis pair to obtain certain $\text{H}_2$ and $\text{CO}_2$ binding energies. One important discovery on 1 is the combinatorial technique with electron donating and electron withdrawing groups; the Lewis pair always bonded to $\text{H}_2$ and $\text{CO}_2$ more strongly when the electron withdrawing group was closer to the base site; the two functional group positions are nonequivalent in 1 when comparing binding energies. However, the problem with 1 is that it either bound $\text{H}_2$ and $\text{CO}_2$ too strongly, or that it bonded to $\text{CO}_2$ more strongly than $\text{H}_2$, potentially poisoning the active site.

Using the trend from 1 and moving on to structure 2, we found that while we increase the strength of the electron withdrawing group, the Lewis pair will bind $\text{H}_2$ more strongly and $\text{CO}_2$ binding energy remains relatively stable. This correlation is true regardless of the electron donating group and the relative stability of $\text{CO}_2$ binding energy can be seen from the red line on Figure 4. The $\text{CO}_2$ binding energy is significantly higher than that of 1 because the distance between the Lewis acid and base site is smaller at 1.70-1.86 Angstroms in comparison to 1’s distance between the Lewis acid and base site of 2.40-2.50 Angstroms, making $\text{CO}_2$ unable to bond well to 2. However, the $\text{H}_2$ binding energy was still too high. This could be due to the structure of 2, which has a dative bond between the Lewis acid and Lewis base.

The trend from 1 and idea of decreasing the distance between the acid and base site from 2 were ways to modify the Lewis pair and help us create 3. At first, we modified 1 so that the nitrogen (Lewis base) was next to the boron (Lewis acid), and the other nitrogen was turned into a carbon. However, due to the double bonded structure of this modified Lewis pair, it was possible for the carbon dioxide and hydrogen to bind to other carbons and R groups. 3 was made so that it still
has a small distance between the Lewis acid and base sites at 1.35 Angstroms, while saturating the carbons with hydrogen so that carbon dioxide and hydrogen can’t arbitrarily bind to R groups and carbon in the Lewis pair structure. 3 was successful because we create a structure where the Lewis acid and Lewis base are next to each other so they lack the distance for CO₂ to bind properly. There also is no dative bond. Overall, 3 bound hydrogen more strongly with increasing strength of electron withdrawing groups on the Lewis acid site, and it couldn’t bind CO₂ well due to the lack of distance between the Lewis acid and base site.

**Conclusion**

Using trends with electron donating and electron withdrawing groups allowed us to tune the Lewis acid site, which helped us get to our net target range for H₂ and CO₂ binding energies. Also, a shorter distance between the Lewis acid and base site and the saturation of the ring structure containing the Lewis pair allowed for H₂ binding that was stronger than CO₂ binding. This information led to the identification of five promising Lewis pair catalysts for industrial use that can be later incorporated in a MOF. Further work needs to be done to test the CO₂ hydrogenation reaction on Lewis pairs. The effect of steric hindrance also could be explored as they should interfere with CO₂ binding on the Lewis pair catalyst. Some further work may include functionalizing the Lewis pairs in MOFs for H₂ and CO₂ storage and calculating the reaction pathways for H₂ and CO₂ binding.

**References**


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