Spring 2015

# New Multiphase Reactor Design Using Electrospun Nanofibers

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Recommended Citation
Smith, Victoria, "New Multiphase Reactor Design Using Electrospun Nanofibers" (2015). *Honors Research Projects*. 21.
http://ideaexchange.uakron.edu/honors_research_projects/21

New Multiphase Reactor Design Using Electrospun Nanofibers

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**Honors Research Project**

Submitted to

*The Honors College*

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Date 4 MAY 2015

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Date 4 MAY 2015

Honors Faculty Advisor (signed)

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Honors Faculty Advisor (printed)

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Dean, Honors College

# New Multiphase Reactor Design Using Electrospun Nanofibers

The University of Akron Honors College
4200:497:002

Victoria Smith

*I affirm that this report represents work performed by me and I assume full responsibility for originality, comprehension, and accuracy of all aspects of the report.*

22 April 2015

# Report Contents

# Executive Summary

The main goal was to create a catalytic fiber to be used for a reaction between hydrogen and phenol to produce as much cyclohexanone, while minimizing cyclohexanol. Electrospun nanofibers were used as the catalytic fiber. The components were:

Phenol + Hydrogen → Cyclohexanone + Cyclohexanol

Where cyclohexanone was the desired product and cyclohexanol was undesired and should have been reduced as much as possible. The reactants were an aqueous phenol solution and hydrogen gas. A main focus was to have the reaction occur room temperature and atmospheric pressure successfully, not only for the ease of production, but also with the cyclohexanone selectivity because heat accelerates the formation of cyclohexanol. Different catalysts tested were Nickel and Palladium, which both worked when stirred in the solution and spun directly into the fiber.

The polymer solutions that were spun and studied included:

1. Ultem via electrospinning on a rotating drum
2. Nylon-6 both electrospinning on a flat sheet and on a rotating drum in a humidity chamber (recommended)
3. 10% PVDF-HFP in Acetone electrospinning with Palladium black or Nickel catalysts in the solution

The electrospun nanofibers samples were wrapped around a metal spring that served as a reactor in the overall design. The spring reactor design improved the reaction rate by decreasing one of the reaction steps. Cyclohexanol was not a desired product and therefore had to be kept at a minimum; an aid to this issue was to keep the temperature low and around room temperature. Using the right catalyst can also stop producing undesirables, hence the demand in this project to develop a method to distribute the catalyst efficiently over the electrospun nanofiber. To immobilize the nanosized catalyst particles, they were embedded into electrospun fibers [6].

As the research continued, the spring reactor was not suitable because the hydrogen gas flow tore the fiber at the inlet and there was not an evenly distributed flow for the reaction to occur. The spring was replaced with a flat sheet reactor. The new set-up brought success; therefore, it is recommended to make a polymer solution with the catalyst, stir it for 24 hours, then electrospin the solution to a nanofibers to use in the flat sheet reactor to produce cyclohexanone.

Analysis programs were Scanning Electron Microscopy (SEM), FibraQuant 1.3, Transmission Electron Microscopy (TEM) and Microsoft Excel. These were used to view fibers, check for the presence of beads, and to measure the fiber diameters. Samples were recently made and submitted for TEM testing and results are currently pending. The samples made were:

- Sample 1: 3 mL PVDF-HFP solution with 0.06g Pd black
- Sample 2: 3 mL PVDF-HFP solution with 0.03g Pd black
- Sample 3: 3 mL PVDF-HFP solution with 0.04g Pd black

The results of the TEM samples will help to fine-tune the appropriate and most efficient amount of catalyst required. As always, there is room for improvement in order to continually optimize this process.

Working on the Honors Research Project throughout the year, I learned about the experimentation and analysis of electrospinning nanofibers. The research of existing technologies and applying them to the lab and gaining hands on experience was invaluable. Running the experiments and learning what works helped the graduate student I was working with. Then learning more about the fibers on a level that was not possible to see with the naked eye was interesting. I have never performed SEM imaging or used FibraQuant 1.3 before this project and the findings proved to be quite useful. Time management was key to completing tasks because the Honors Project was not structured to show in the weekly schedule with my other courses, but the work had to be completed and reported. Overall, I gained knowledge and methodologies that I otherwise would not have without this project.

# Introduction

An important polymer reaction is the hydrogenation of phenol to produces cyclohexanone. There is a high demand for cyclohexanone as it serves as an intermediate for materials, commonly for Nylon-6 and Nylon-6,6, which millions of tons are used each year. The current technology takes the electrospun sample and coats it with Palladium catalyst in order to complete the reaction as the $H_2$ passes through the polymer and spring to the liquid phenol. However, observations have been made that there was not an efficient amount of catalyst being used and not dispersed well. The unique idea that was under development was to take the spring of the electrospun nanofiber and have the hydrogen flow through the center of the tubular spring while the phenol solution flows on the outside, with the nanofiber mat holding catalyst separates the two phases. The main routes for optimization are going to be the ways to mechanically process the $H_2$ for the hydrogenation of phenol (liquid) to cyclohexanone from the reactions below.

$$\text{Phenol} + H_2 \rightarrow \text{cyclohexanone} + \text{cyclohexanol} \tag{1}$$

$$\text{Phenol} + 2H_2 \rightarrow \text{cyclohexanone} + H_2 \rightarrow \text{cyclohexanol} \tag{2}$$

The goal of this part of the project was to improve a reactor using an electrospun nanofiber. The main issue of the current status of this project occurred when the $H_2$ flows from the source and through the top of the hex nut to be delivered to the inside of the spring coated with nanofiber, the polymers tend to break. The source of hydrogen can be either a liquid or gas. If it is in the liquid form, it comes via formic acid-2-propanol, ethanol, and methanol. In this experiment, hydrogen gas was used. There were a few parameters that would be easiest to primarily change including:

1. Change the grams per meter squared (gsm) of polymer and the time of the electrospinning
2. Adjust $H_2$ flow rate in the reaction
3. Change the polymer itself
4. Use another metal

Different methods for the testing analysis included Scanning Electron Microscope (SEM) and the software FibraQuant 1.3 mainly analyzing the fiber diameter and for beads to measure the success of the process.

One uncontrollable limitation was the humidity as it has an effect on electrospinning the Nylon-6. The target was to have it between 30-40%, but the weather and air conditioning/heating was not in control of the lab. Human error was another limitation in consistency of the results; therefore experimental procedures were in place. Limitations lie in the reaction set up and the catalyst selection.

# Background

## Reaction

Cyclohexanone is a valuable intermediate produced via the gas phase hydrogenation or the more preferred liquid phase hydrogenation of phenol. Phenol can be hydrogenated in either a one or a two-step process; the one-step process is preferred since it is easy to operate, eco-friendly, and has a higher selectivity towards cyclohexanone. [1] There is a further hydrogenation step that is more difficult when recovering the cyclohexanone due to the low selectivity from cyclohexanone to cyclohexanol. [1] Therefore, a palladium catalyst is used via electrospinning; specifically $Pd/Al_2O_3$, $Pd/TiO_2$, $Pt/TiO_2$, and Pd/PEI were prepared in literature.

One variable was the catalyst in the polymer. The way the catalysts were used in this project was for support via polymer, others are activated carbon, $Al_2O_3$, and $TiO_2$. Another way is catalytic metal, which is when it comes as a precursor. Then one converts the precursor into the active metal. Nickel and Palladium were the main two elements tested. Palladium comes from $PdCl_2$ (other forms are available), during calcination is then heated at 600°C for 4 hours to get PdO.

$$\frac{1}{2} O_2 + PdCl_2 \rightarrow PdO$$

Then Hydrazine ($N_2H_2$) would be added to reduce the PdO to get Palladium. The complete reaction is presented below.

$$N_2H_4\ (l) + 2PdCl_2 \rightarrow N_2\ (g) + 2Pd^0\ (s) + 4HCl$$

Another mechanism to achieve Pd is to again start with $PdCl_2$ and add Sodium Borohydride to get Pd.

To use a metal precursor, it needs to be reduced to a metal particle and can be reduced by using gas reducing agent or a liquid reducing agent.

$$\text{Reducing Agent + Metal Precursor (salt)} \rightarrow \text{Metal Particle + Water + Other Salt (typically)}$$

In this research, Sodium Borohydride was dissolved in a liquid source.

## Electrospinning

Electrospinning starts with a droplet of polymer solution, collector. The word “electrospinning” stems from “electrostatic spinning” [11]. In this lab setting, the grounded collector is a rotating wire spring and a grounded foil behind the spring.

Electrospinning of a polymer with small catalyst particles blended in the solution produces fibers with embedded particles; this approach immobilizes the nanoparticles [6].

### Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)

Both SEM and TEM were used in characterization of polymer samples. SEM was used to measure fiber width and TEM was used to measure particle size and combines all particles. SEM images are provided within this report, however, the TEM results are still pending.

## Hypothesis

Nanosized catalyst particles on electrospun nanofibers should be able to convert at rates comparable to large catalyst particles to help with the reaction:

Phenol + Hydrogen → Cyclohexanone + Cyclohexanol

The goal of the reaction is to have a high selectivity for cyclohexanone and minimize the amount of cyclohexanol. Reaction at room temperature and atmospheric pressure would be a huge improvement, not only with ease of production, but also with the cyclohexanone selectivity because higher temperatures favor the formation of cyclohexanol.

Testing various electrospun catalysts (Nickel and Palladium black) and different polymer solutions (Ultem, Nylon-6, and PVDF-HFP) to form fibers provides information to help optimize the design.

From this overall scope, this research and report focused on the reactor design and catalytic nanofiber that would best convert phenol and hydrogen to cyclohexanone.

# Experimental Methods

## Reactor

The hydrogen was fed as a gas and the phenol was in liquid form. Phenol was dissolved in water to make a 20-g/L aqueous phenol solution. Typically, a 400mL solution was made consisting of 8g phenol dissolved in 400mL of water.

Initially, the reactor experiment was to occur with the metal spring serving as the reactor, as demonstrated in the silicon glue preparation in Figure 1 below. The spring was prepared one day prior to experimentation to ensure a completely dry and sealed connection for the spring apparatus. The apparatus consisted of a spring, hex-nut, rubber stopper, wrench, and silicon glue. The procedure explained to clean the metal with water and dry, and then to apply silicon glue.

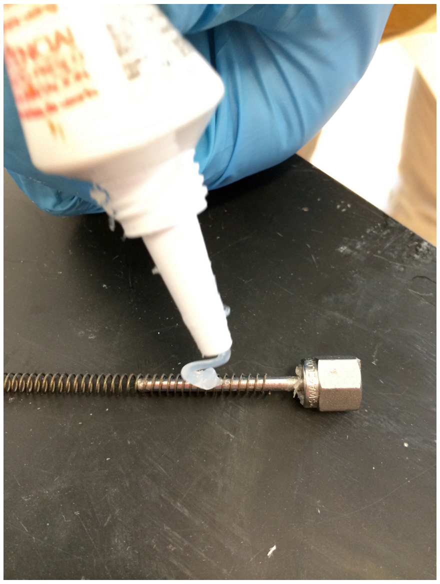


**Figure 1. Apply silicon glue to the spring apparatus and spread with gloved hands for a smooth, even coat and allow to completely dry overnight.**

Once coated with a layer of catalytic electrospun fibers, the spring apparatus was submerged appropriately into the water. The hydrogen flowed at 2-3PSI, but the hydrogen bubbles only went to the top and bubbled out instead of passing through the whole spring. Consequently, the flow rate was too high, the polymer was too weak, or possibly the design or materials needed modification, and the issue needed to be addressed. The first adjustments were the flow and the initial ramp-up flow rates were adjusted several times, but inevitably the fiber tore at the top.

The polymer and reactor design were the main components needed for a successful reaction. The methodology of the experiment slightly changed as the research progressed. The chemicals remained consistent, but the reaction set-up had to be adjusted for the reaction to work properly. The reactor changed from the spring apparatus to a flat sheet reactor displayed in Figure 2, below.

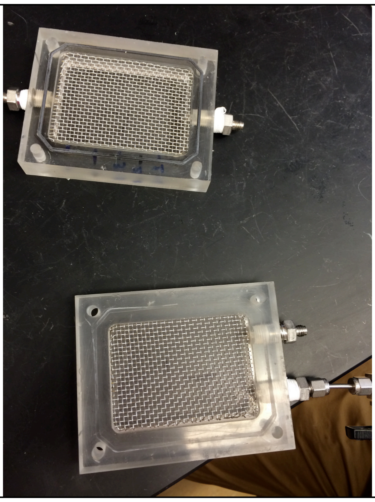
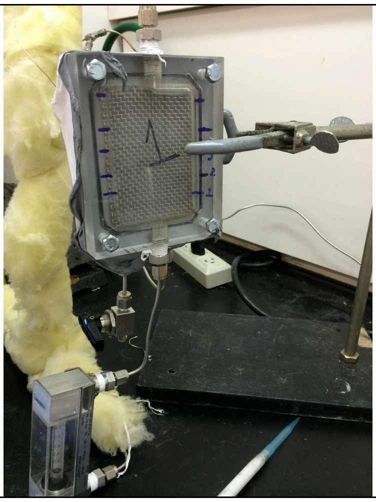
| | |
|---|---|
|  |  |
| Reactor in the preparation stage. | Same reactor in reaction stage with sheets in place. |

**Figure 2. Flat sheet reactor.**

In the preparation stage, the electrospun nanofibers sheet was placed between the two plates as smoothly as possible. Then the plates had screws at the 4 corners to keep the device together during the reaction, tautly holding the fiber mat in place. The hydrogen flowed from the bottom to the top. The reactor was then placed in the overall set up, which includes the water and hydrogen gas connections.

Afterwards, the procedure called for the water to be plugged in and to fill the top left container with DI water. The water flow started with the tip valve open so that the flow will go into the waste jar. The top valve would be closed to push water and have the flow meter start high, then reduced it to 0.2 L/hr until it was consistent; then the waste drops were collected from top of the flow meter where wire dropped from top of flow meter while the wire served as a recycle in the top compartment. Then removed the wire and completely emptied the water from the system.

The reactor was connected with the hydrogen flowing from bottom to top. The hydrogen went in the bottom, passed through the fiber sheet, and then the top outlets were product, phenol, and the third outlet was closed. Always with the hydrogen generator, it was important to have the high pressure initially and then bring it down to a consistent, low setting at 50 PSI. Then hook it up because otherwise the high-pressure flow could break the fiber sheet and ruin the experiment. The pressure was not as large of a concern when shutting down. The hydrogen flow should be at 100 mL/min at 50 PSI and the phenol 0.25 L/hr.

The first solution tried with the new set up was 20wt% Nylon-6 that was spun in the humidity chamber on the rotating drum. The composition was 20wt% Nylon-6, 40wt% of <99% Acetic Acid, and 40wt% of 98% Formic Acid.

Within the reactor the hydrogen passed on the same side of the liquid phenol and passed through the nanofiber layer for the reaction.

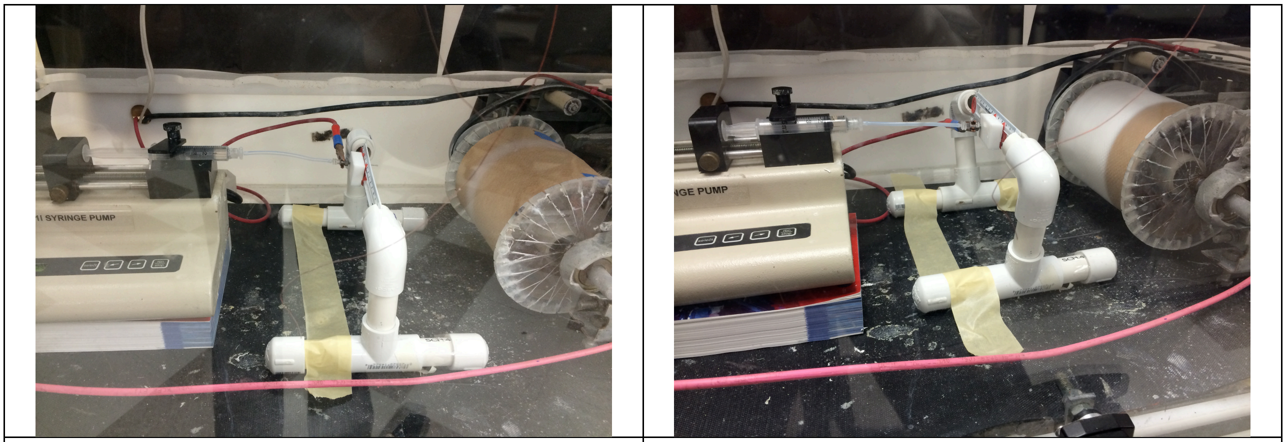
## Electrospinning

Pertinent information can also be found in the *Background*, *Electrospinning* section of this report.

The main polymer solutions were created with the according methods:

1. Ultem was spun via the rotating drum method in the fume hood.
    a. Voltage at 25 kV
    b. Flow rate of 25 μL/min
    c. Distance of 20 cm
    d. Approximately 4 hours

2. Nylon-6 was spun via the rotating drum within the humidity chamber.
    a. Voltage 25 kV
    b. Flow rate of 9.1 μL/min
    c. Distance of 9 cm
    d. Move needle 2 cm every hour over a 4 hour time span



| Initial spinning of 20 wt% Nylon-6 in the humidity chamber. | Needle moved across the bar to neatly expand the fiber sample. |
|---|---|

**Figure 3. Electrospinning 20 wt% Nylon-6 in the humidity chamber.**

3. PVDF-HFP was spun as a flat sheet.
    a. Voltage 30 kV
    b. Flow rate of 15 mL/hr
    c. Distance of 15 cm

The polymer solutions were created and stirred 24 hours prior to electrospinning.

When electrospinning sheet samples for the reactor, the foil was cut according to a template and then the foil had to be completely smooth in efforts to create a flat sample and a sufficient surface area to react.

During the spinning process, it was important to clean the needle from collections of polymer that could hinder the process or clog the system. Also when refilling the 5 mL syringe, first stopped the pump, pulled the sheet away, and then turned off the voltage because this would help to minimize the amount of droplets that could hinder the sufficiency of the sheet. A good sample would be as evenly distributed as possible, no holes poked through, and was thick enough to pull away from the foil in one continuous piece.

## Testing PVDF-HPF properties

In search of PVDF-HFP capabilities, a sample of PVDF-HFP fiber was placed in a furnace at 120°C, Figure 4.

**Figure 4. Fiber sample of PVDF-HFP to test various properties.**

Another PVDF-HFP fiber sample was placed in a jar with Hydrazine Monohydrate. Even though the prediction was for the sample to dissolve, the fiber sample remained intact. Utilizing this solution, a small amount of Nickel (II) Acetate Tetrahydrate (solid) was added with a scoopula and a color change was observed. The turquoise powder changed the solution to indigo and then when the solution was stirred the chemicals were dispersed, the solution was purple. The solution was then taken to the fume hood and was stirred in order to ensure that the fiber did not dissolve. The reaction was not exothermic. Further studies could be very useful from this finding. The fact that the fiber did not degrade in the hydrazine was a great finding because if hydrazine were used to get palladium catalyst, it would not be desirable to have the fiber break down during the reaction.

# Data and Results

## FibraQuant 1.3 & Microsoft Excel

Images were uploaded to FibraQuant 1.3 software for analysis and the measurement results were exported to Microsoft Excel to develop histograms and calculate average diameter size.

Finding the best composition of HTAB in the Ultem polymer solution will contribute to optimization for the reaction. Four solutions in 0.5% increase were made and analyzed from 0% to 1.5% HTAB in Ultem. The average fiber size was the smallest with 0.0% HTAB in Ultem and was largest with 0.5% HTAB in Ultem; all results are listed in Table 1, below.

**Table 1. Varying amounts of HTAB in Ultem.**

| HTAB | Average Fiber Size (um) | Standard Deviation |
|---|---|---|
| 0.0% | 0.234 | 0.257 |
| 0.5% | 0.861 | |
| 1.0% | 0.570 | |
| 1.5% | 0.512 | |

Utilizing FibraQuant 1.3, samples numbered “2-5” were analyzed for the sample containing 0.3g PtIr Black in 15mL PVDF-HFB and the average fiber diameters are displayed in Table 2 below.

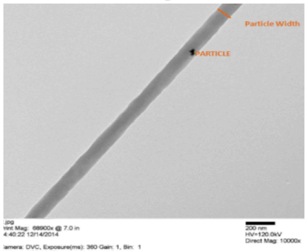
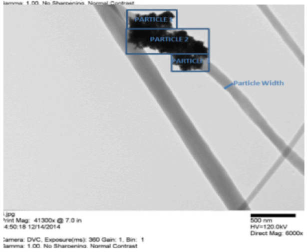
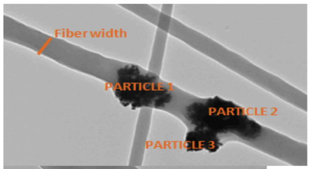
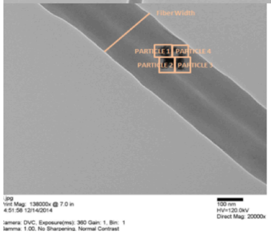
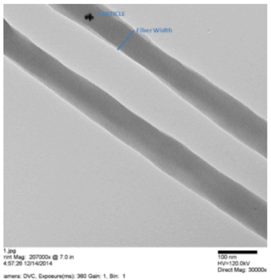
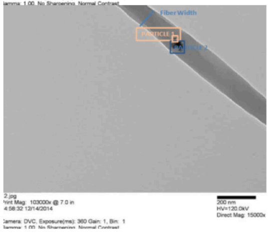
**Table 2. 0.3g PtIr Black in 15 mL PVDF-HFP.**

| Sample | Average Fiber Diameter (µm) | Standard Deviation |
|---|---|---|
| 2 | 0.306 | 0.019 |
| 3 | 0.278 | |
| 4 | 0.282 | |
| 5 | 0.318 | |

Samples containing 0.15g Pt Black in 15mL PVDF-HFB was analyzed via SEM imaging and FibraQuant 1.3 with the results displayed in Table 3, below.

**Table 3. Summary of analysis of results for 0.15g Pt Black in 15 mL PVDF-HFP.**

**Summary of Analysis Results for 0.15g Pt black in 15 mL PVDF-HFB**

| | | Average Values of Analysis Measurements | | | | |
|---|---|---|---|---|---|---|
| Image | Image # | Fiber Width (µm) | Particle 1 Width (µm) | Particle 2 Width (µm) | Particle 3 Width (µm) | Particle 4 Width (µm) |
|  | 2 | 0.110 | 0.016 | | | |
|  | 5 | 0.119 | 0.133 | 0.254 | 0.166 | |
|  | 6 | 0.112 | 0.109 | 0.118 | 0.114 | |
|  | 8 | 0.231 | 0.044 | 0.036 | 0.030 | 0.014 |
|  | 11 | 0.076 | 0.010 | | | |
|  | 12 | 0.120 | 0.006 | 0.029 | | |

## Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)

SEM images were analyzed for 20 wt% Nylon-6 samples and are displayed in Figures 5, 6, and 7.

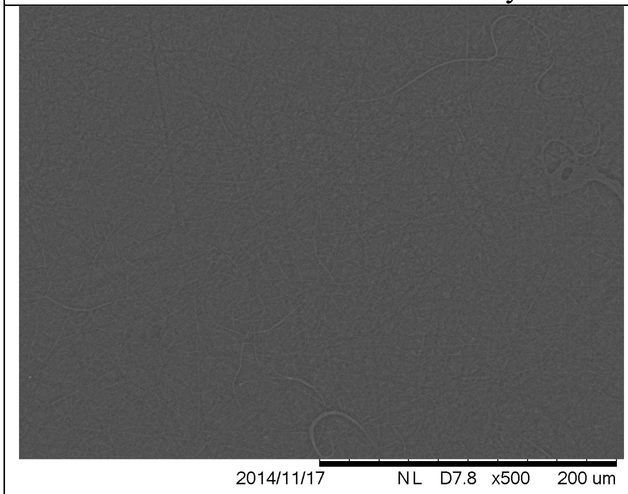
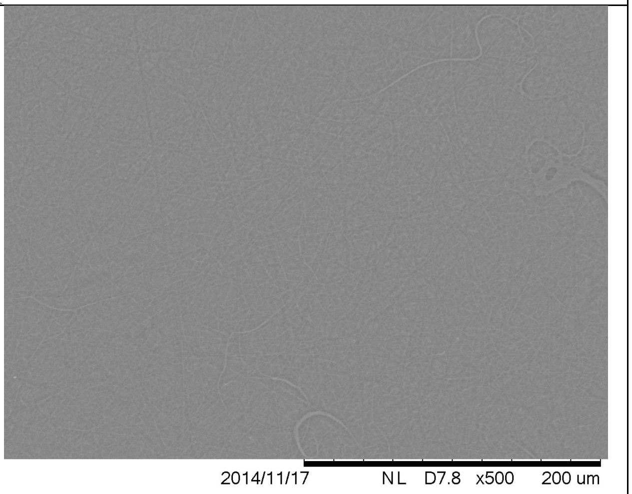
<table>
<tr><td colspan="2">20 wt% Nylon-6 sample from 11/12/2014</td></tr>
<tr><td> </td><td> </td></tr>
<tr><td>Magnification: 500x<br>Darker light setting</td><td>Magnification: 500x<br>Lighter light setting</td></tr>
</table>

**Figure 5. SEM images of 20 wt% Nylon-6.**

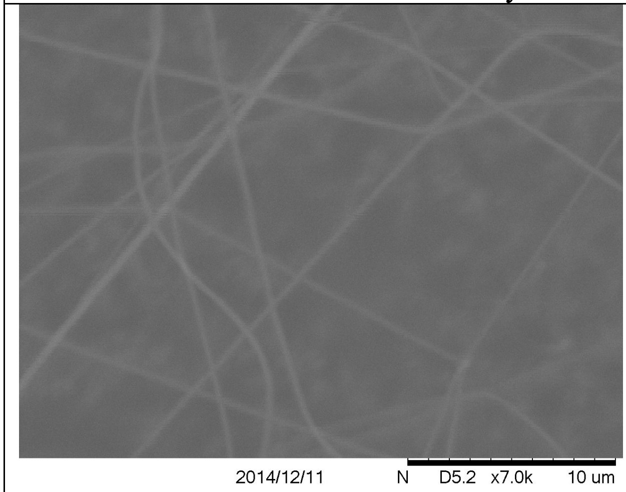
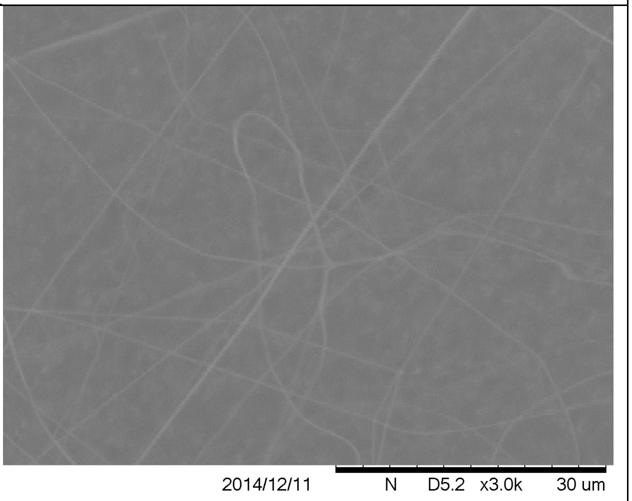
<table>
<tr><td colspan="2">20 wt% Nylon-6 sample from 11/19/2014</td></tr>
<tr><td> </td><td> </td></tr>
<tr><td>Magnification: 7000x</td><td>Magnification: 3000x</td></tr>
</table>

**Figure 6. SEM images of 20 wt% Nylon-6.**

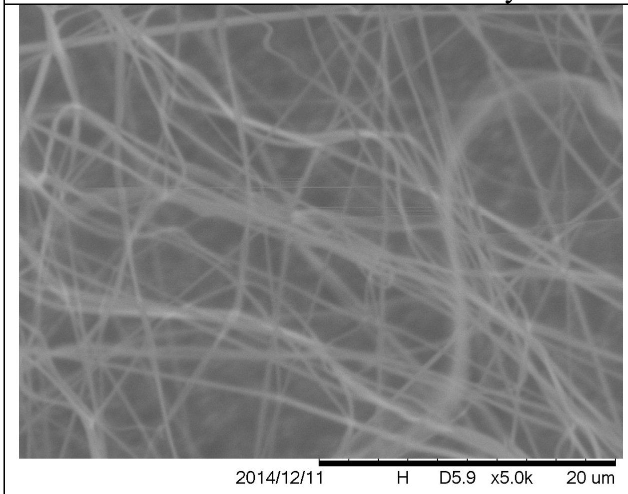
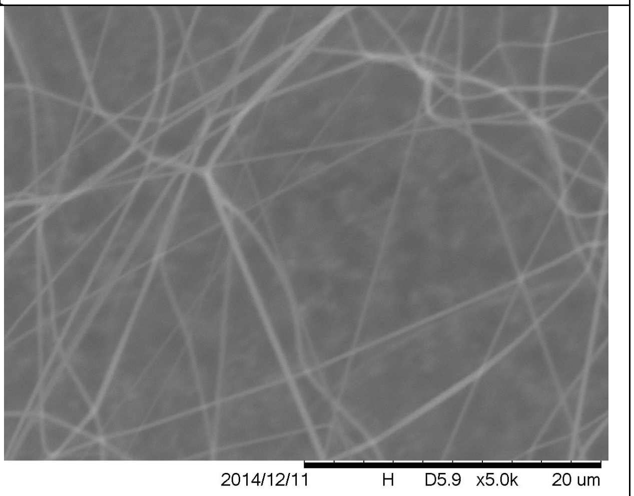
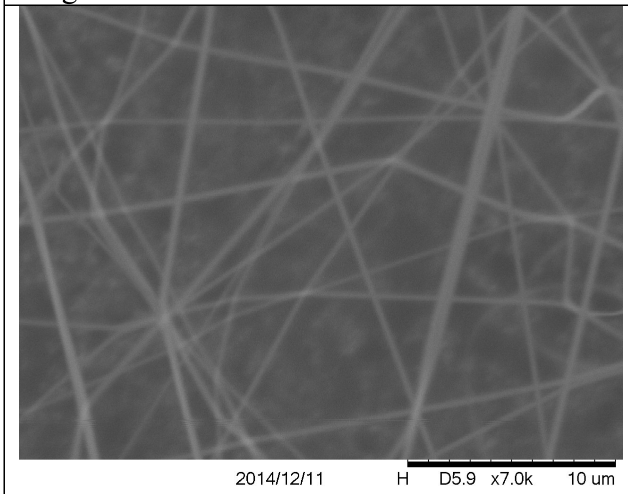
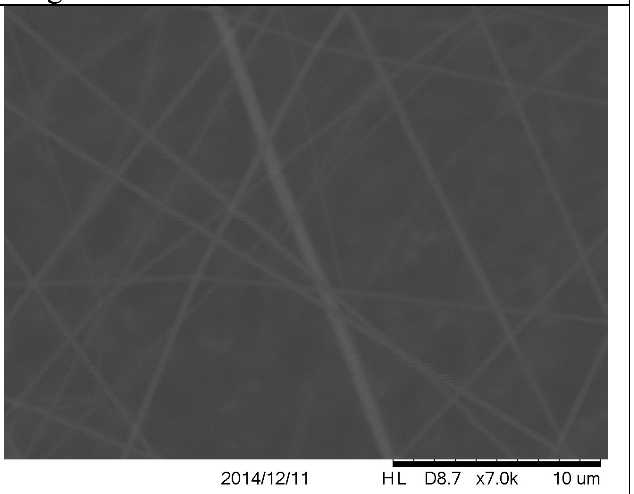
| 20 wt% Nylon-6 sample from 11/21/2014 | |
|---|---|
|  |  |
| Magnification: 5000x | Magnification: 5000x |
|  |  |
| Magnification: 7000x | Magnification: 7000x |

**Figure 7. SEM images of 20 wt% Nylon-6.**

SEM images of PVDF-HFP without catalyst and PtIr/PVDF-HFP with catalyst in the solution were analyzed and compared. The fiber sheet that only contained PVDF-HFP was white, tracing back to the PVDF-HFP powder being white in color. The sheet with the PtIr addition was gray since PtIr was originally black. All images were taken in COMPO mode at 15 kV. The magnification levels were x1200, x1500, and x3000. The samples were taken from different areas on each respective sheet. For comparison, the conditions remained at the same settings and were taken at the same magnification levels for both fiber samples. The results are presented in Figures 8 and 9.

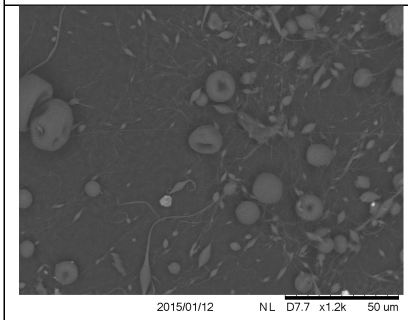
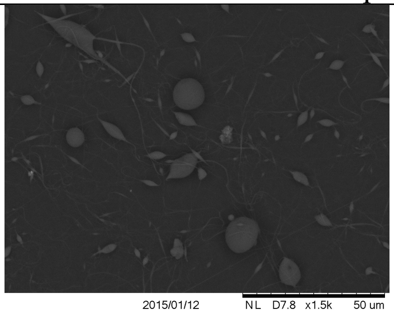
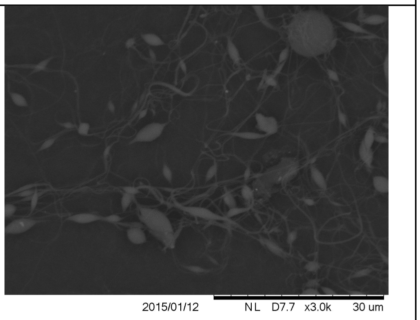
<table>
<tr><th colspan="3">PVDF-HFP white fiber sample</th></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td>Magnification: 1200x</td><td>Magnification: 1500x</td><td>Magnification: 3000x</td></tr>
</table>

**Figure 8. SEM images of PVDF-HFP fiber without catalyst.**

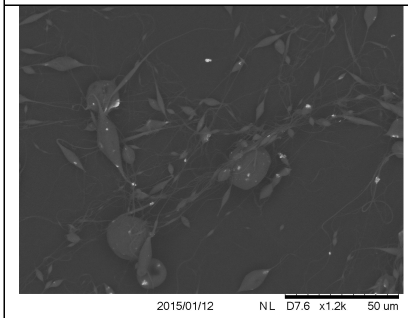
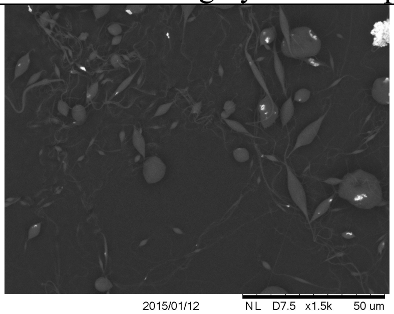
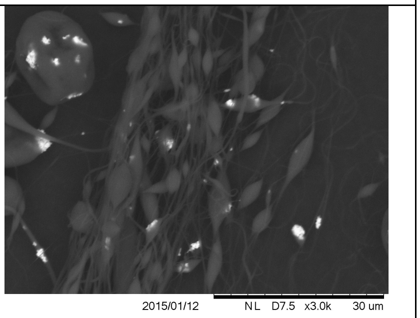
<table>
<tr><th colspan="3">PtIr PVDF-HFP gray fiber sample</th></tr>
<tr>
<td> </td>
<td> </td>
<td> </td>
</tr>
<tr><td>Magnification: 1200x</td><td>Magnification: 1500x</td><td>Magnification: 3000x</td></tr>
</table>

**Figure 9. SEM images of PDVF-HFP fiber with catalyst.**

Samples were made for TEM testing and results are currently pending. The samples made were:

- Sample 1: 3 mL PVDF-HFP solution with 0.06g Pd black
- Sample 2: 3 mL PVDF-HFP solution with 0.03g Pd black
- Sample 3: 3 mL PVDF-HFP solution with 0.04g Pd black

The results of the TEM samples will help to fine-tune the appropriate and most efficient amount of catalyst required.

# Discussion/Analysis

## Reactor

A decision was made to change the reaction set up from the spring to the flat sheet. The hydrogen gas feed was too much for the spring and would tend to tear at the top. Furthermore, the distribution of hydrogen was not balanced and the bottom of the spring did not have as much hydrogen for the reaction, but the flow could not be increased to reach it because it would affect the top.

With the flat sheet, if the contact angle was greater than 150, then it is considered super hydrophobic, if the angle is greater than 90, then it is hydrophobic, and if the angle is less than 90, then it is hydrophilic.

## Electrospinning

At the beginning stages of the research, the Nylon-6 compositions created and analyzed were 6 wt%, 12 wt%, and 20 wt% and were electrospun on flat sheets. The samples did not spin well and the polymer solution had speckle on the sample, showing visible bumps and clumps.

In one trial, two solutions were made: 6 wt% and 12 wt% Nylon-6. The parameters set were a flow rate of 0.002 mL/min, 25 Volts, Aluminum foil for the collector, and the distance was 20 cm. When the experiment was analyzed for results the next day, the notches were broken on the needle side, shown in Figure 10. The polymer solution dripped out instead of being electrospun. Some still spun, but not a usable amount.

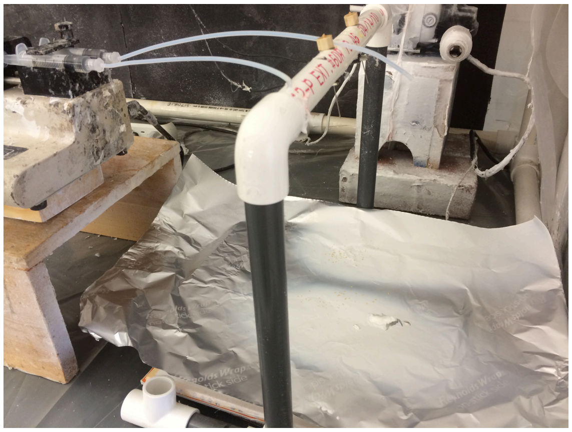


**Figure 10. Sample of Nylon-6 from 10/17/2014 that inspired the 90-degree direction angle change for the nozzles not to break.**

In order to problem solve, the orientation of the rod angle was changed 90 degrees so that the needles were horizontal instead of vertical in order to relieve all stress and tension from the harsh angle, visually demonstrated in Figure 11.

**Figure 11. Sample from 10/17/2014 with the rearranged set up with the needles on a horizontal plane.**

After some run time, the set up worked better, shown in Figure 12. It ran completely with careful monitoring.

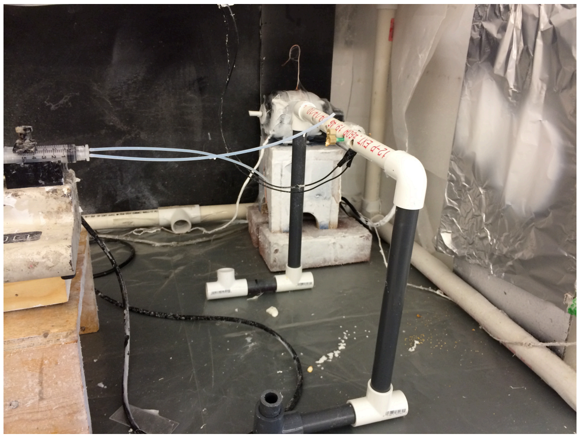


**Figure 12. Sample from 10/20/2014 polymer solution, set up, but the materials (plastic male/female tube parts and polymer solution) were not compatible.**

The system had the same settings, but the needles were set to the horizontal plane because it worked better than the vertical spinning and did not break the nozzles. The 12 wt% solution was more successful.

Subsequent to this, a discussion led to changing the polymer and the method of making the material. The method of Electrospinning 20 wt% Nylon-6 with Formic Acid and Acetic Acid in a humidity chamber was the adopted alteration. Humidity was a major contributor to the quality of electrospinning Nylon-6. Humidity varied due to the weather changes and due to the building heating system.

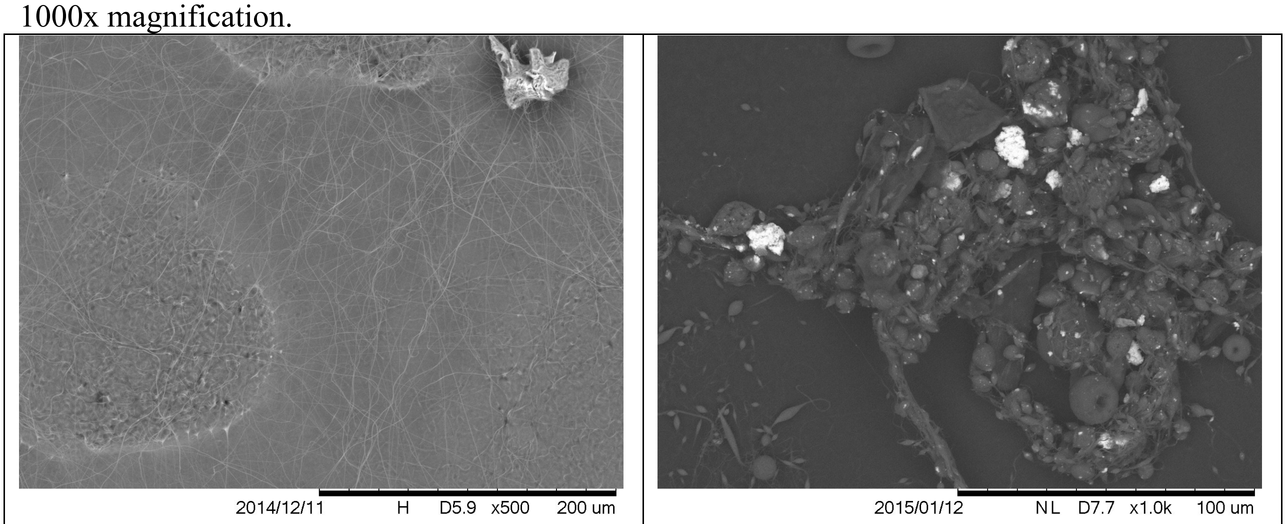
Another observation was when other colleagues were electrospinning nearby, the fiber for this work tended to spin more aggressively and sometimes drifted away from the desired collector, as shown in Figure 13, below.

**Figure 13. Demonstrates the observation that the environment influences electrospinning environments. Also when there is an experiment occurring at the same time, the sample may turn cobweb like this sample**

A wood plank was placed between the two electrospinning stations experiments in effort to reduce the drift. On several occasions, the polymer was spun overnight, there was polymer covering the entire workspace, similar to cobwebs meaning that the flow rate was too low, the voltage was too low, or the distance between the needle and the foil collector was too far apart.

In one test, 2 layers of 5 mL solution each time (10 mL polymer used total) were electrospun. The gray fiber sample contained Pd black, was thicker and came off of the foil more easily. The white sample was too thin the first time, therefore a new sample had to be made. Then the second sample was made with 2 layers of 5 mL solution used each layer. This sample peeled off the foil significantly better and was used for the reaction. The trouble may have stemmed from human error, as it was the first time creating that solution.

Sometimes when analyzing the fiber samples, there were strange portions of clumping and bubbles. Figure 14 provides examples of such cases; on the left was one found in Nylon-6 made in the humidity chamber at 500x magnification and on the right was one found in PVDF-HFP at 1000x magnification.



Strange clumps in a 20 wt% Nylon-6 sample. | Interesting cluster a PVDF-HFP sample.

**Figure 14. Curious findings in fiber samples during SEM analyses.**

# Conclusions and Recommendations

## Reactor

Use the flat sheet reactor set-up instead of the metal spring. The hydrogen was able to pass through the fiber sheet without ripping it and the gas was dispersed more uniformly.

Explore the opportunities with hydrazine as a hydrogen donor to hydrogenate the unsaturated components [24]. Use $PdCl_2$ as the Palladium precursor to achieve Pd catalyst, then convert it to PdO while calcination, then use hydrazine to have PdO reduce to Pd.

## Electrospinning

The polymer solution should be made 24 hours prior to electrospinning. While the polymer is spinning, be sure to monitor the needle and to keep it clear of collections of polymer hindering the needle end clogging the system. When it is time to refill the 5 mL syringe, stop the pump, pull the sheet away, and then turn off the voltage to reduce the amount of droplets on the sheet that could break the fiber sample. Also be mindful of air pockets in the syringe, which cause a small spray of polymer onto the fiber sheet and the liquid can create small holes in the overall sheet. Following this advice should provide a well distributed, thick, and successful fiber for the sheet reactor scheme.

When electrospinning Nylon-6, do so in a humidity chamber on a rotating drum for the best results. The composition recommendation is 20 wt% Nylon-6 in Formic Acid and Acetic Acid.

SEM imaging can use carbon tape or copper tape. Carbon tape was used in all analyses. The contrast with the black helps with image analysis.

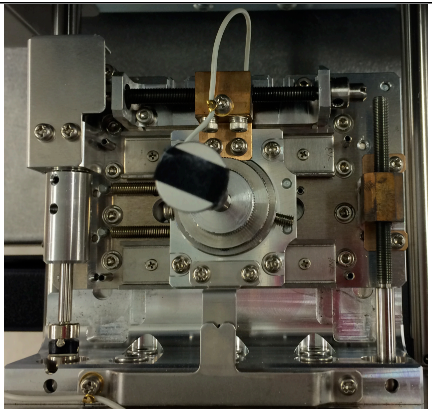
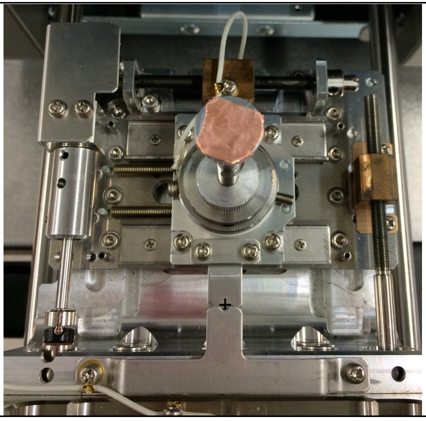
| | |
|---|---|
|  |  |
| SEM imaging with carbon tape, used for all experiments in this report. | SEM imaging with copper tape, which was not used due to low quality results with the samples tested. |

**Figure 15. Carbon tape stage vs. copper tape stage.**

The overall best polymer solutions to electrospin nanofibers were Ultem, Nylon-6, and 10% PVDF-HFP in Acetone. Furthermore, the catalysts tested were Palladium black and Nickel. A recommended procedure is:

1. Make the desired polymer solution with the catalyst and allow the solution to stir on a magnetic stir plate at room for 24 hours
2. Electrospin 15 mL total solution on a flat sheet by filling a new, clean 5 mL syringe 3 times
    a. Flow rate at 25
    b. Distance at 15 cm
    c. Voltage at 30 kV
3. Make a liquid phenol solution
4. Run the flat sheet reactor scheme for the reaction

## Safety

Main chemicals used throughout this segment of research are listed below.

1. Nylon-6
    a. Formic Acid (98%)
    b. Acetic Acid (>99%)
2. PVDF-HFP fiber
    a. Poly(vinylidene fluoride-hexafluoropropylene) PVDF-HFP
    b. Acetone
3. Ultem
    a. Polyether imide (PEI)
    b. Trichloro ethane (TCE)
    c. Hexadecyl Trimethyl Ammonium Bromide (HTAB, surfactant)
4. Catalysts
    a. Palladium black (Pd black)
    b. Nickel (II) Acetate Tetrahydrate (Ni catalyst)
5. Other
    a. Hydrazine monohydrate

Personal protective equipment (PPE) included safety glasses, long sleeves, long pants, closed toe shoes, and a disposable facemask to prevent breathing in harmful fumes.

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