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# Aerobic Processing of Glycerol

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# Aerobic Processing of Glycerol

A Major Qualifying Project  
Submitted to the Faculty of  
Worcester Polytechnic Institute  
in partial fulfillment of the requirements for the  
Degree in Bachelor of Science  
In  
Chemical Engineering  
By:

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Michael Chin

4/30/2015  
Project Advisors:

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Marion Emmert

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## **Abstract**

Biodiesel is looked to as an alternative to fossil fuels. With an ever increasing production of biodiesel comes a byproduct of glycerol. Due to the amount of glycerol being produced, it is no longer a commodity. This report looks into changing glycerol into a higher valued chemical, dihydroxyacetone as to incentivize industry to continue increasing production of biodiesel. This was achieved by the catalytic oxidation of glycerol using a palladium catalyst under aerobic conditions.

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## 1. Introduction

Fossil fuels will eventually be depleted.<sup>1</sup> There is only a limited supply of fossil fuels such as coal, oil, and natural gas. These were created over millions of years through the decomposition of organic life. Alternatives need to be found to replace fossil fuels to power the world we live in as the consumption of energy continues to increase shown in Figure 1.<sup>2</sup> Fossil fuels, (petroleum, natural gas, and coal), are the biggest source of energy for the United States, and the consumption of these fuels are growing at an unsustainable rate. Alternatives such as solar, air, nuclear, or biofuels are currently under investigation as sustainable energy alternatives to replace fossil fuels to lessen our dependence on these fuels.<sup>3</sup>

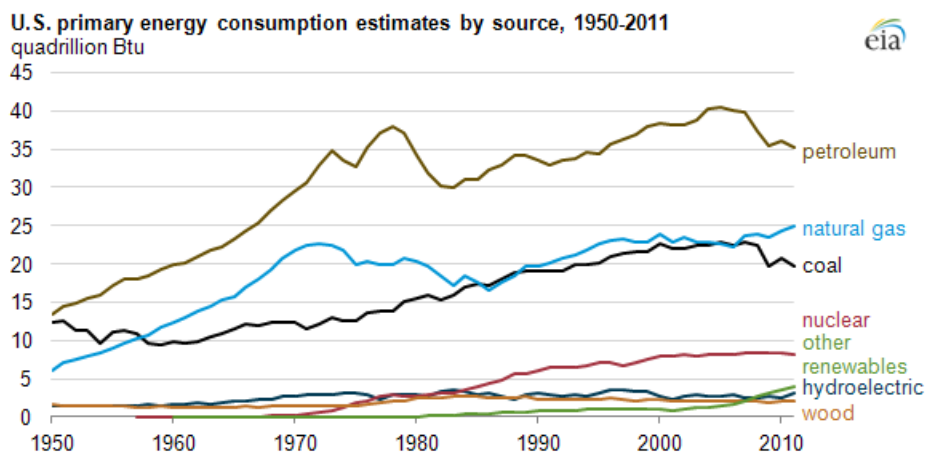


Figure 1 U.S. Energy Consumption from 1950-2011<sup>2</sup>

Renewable resources are resources that can be consumed and produced at equal rates where it is sustainable to be used. Fossil fuels are not renewable because we cannot reproduce the fossil fuels once they are consumed. Solar, air, nuclear, or biofuels are resources that we can endlessly use to produce energy.

### 1.1 Biofuels

Biofuels are considered to be a suitable alternative to diesel gasoline because biodiesel does not need to be altered as it is already equipped to be used in diesel engines. This is due to the similar

chemical structure of biodiesel, shown in Figure 2, to the structure of diesel, shown in Figure 3. Both are made of a long carbon chain except biodiesel has an ester functional group attached to the end of the chain. With a similar energy density of biodiesel to diesel, biodiesel can replace diesel in most applications without modification. Production of biodiesel continues to increase every year due to changing opinions in the government and public that are looking into alternative energies to remove our dependence on fossil fuels. In 2013, 1 billion gallons of biodiesel, was produced compared to the 460 million gallons produced in 2012.<sup>4</sup> Biodiesel, **3** (Scheme 1), is produced through the esterification of triglycerides, **1**, from different vegetable based oils such as soybean, corn, and algae. During the synthesis of biodiesel, glycerol, **4**, is also produced as a byproduct in almost 10 wt.%.<sup>1</sup>

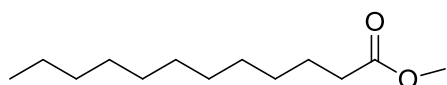


Figure 2 Biodiesel

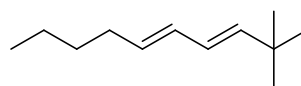
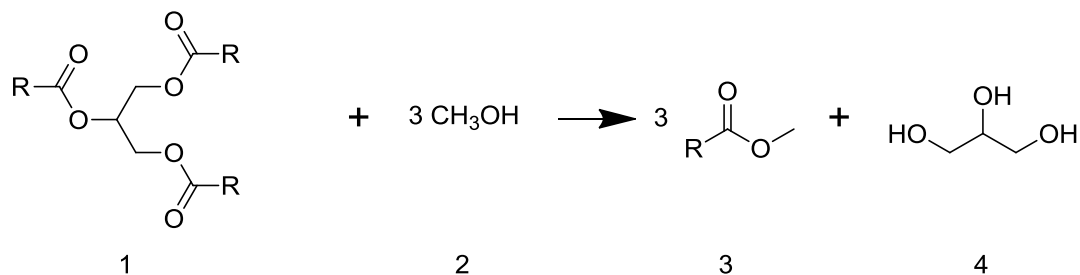


Figure 3 Diesel



R: carbon chains

**Scheme 1** Esterification of triglycerides to produce biofuels.

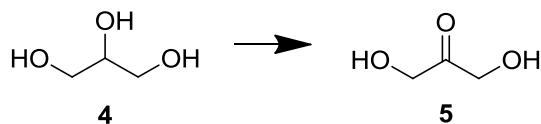
## 1.2 Glycerol

The abundance of glycerol produced has diminished the market with the supply of glycerol being more than the demand, therefore dropping the price of crude glycerol by more than 50% from \$500/ton in 2008 to \$220/ton in 2010.<sup>5</sup> Every year, 160,000 tons of glycerol is used in the pharmaceutical, food, and tobacco industries as additives to make the products sweeter,

smoother, or as a solvent<sup>2</sup>. The demand cannot keep up with the supply of glycerol, so it is now considered a waste product instead of a valuable product as there is no longer the demand for the excess glycerol. Glycerol, as a large by-product of the production of biofuels, is reducing the profits that would convince companies into producing biofuels. Finding a way to commercialize glycerol as a profitable product or starting material for other products would encourage companies to increase the production of biofuels in order to supplement the fossil fuels the world depends upon.

### 1.3 Dihydroxyacetone

Dihydroxyacetone, **5** (scheme 2), is a commercially viable product, produced from the oxidation of glycerol. Dihydroxyacetone is mainly used in cosmetic products as a skin tanning agent, that has a higher commercial value at \$150/kg compared to the depressed value of glycerol \$220/ton.<sup>5</sup> Current practices to produce dihydroxyacetone are through fermentation of glycerol via microbes<sup>6</sup>. However, this approach is problematic due to the high costs of production (time) and low yields (less than 60 %). This technique is being used because of the strict requirements of good manufacturing practices regulated by the FDA that need to be met for use in the cosmetic industry; there should not be any excess hazardous materials from production to prevent human endangerment. Alternative techniques are being investigated through mild catalytic oxidation to produce dihydroxyacetone which meet the regulations of the cosmetic industry.



**Scheme 2** Oxidation of glycerol to dihydroxyacetone

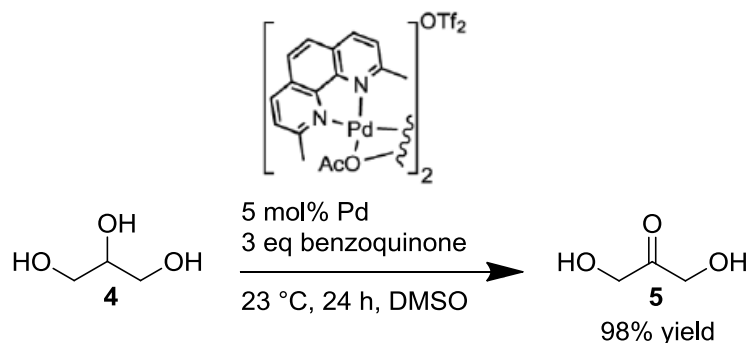
#### 1.3.1 Catalytic Synthesis of Dihydroxyacetone using a Palladium Catalyst

Palladium catalysts have been previously studied for the oxidation of glycerol. Studies by the Waymouth group have investigated the oxidation of glycerol with neocuporine palladium acetate

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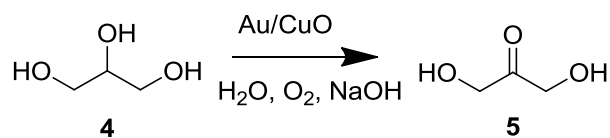
catalyst (6) with benzoquinone as an oxidizer shown in Scheme 3.<sup>7</sup> From initial testing with just the catalyst at 23 °C in DMSO, low yields of 36 % for dihydroxyacetone were achieved. Using benzoquinone as an oxidant with the palladium catalyst, 99 % yield was observed.<sup>8</sup> This method produces promising results, but would not be suitable for the cosmetics industry, since benzoquinone is toxic to humans and aquatic life good manufacturing practices suggests to avoid using the chemical to prevent any chance of contamination.<sup>6,9</sup>



**Scheme 3** Palladium catalyzed oxidation of glycerol to dihydroxyacetone.

### 1.3.2 Catalytic Aerobic Oxidation using Gold Catalysts

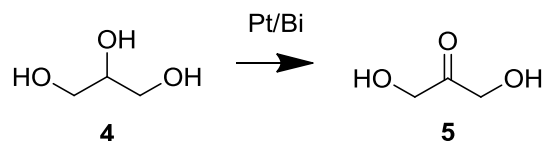
Mild reaction conditions for producing dihydroxyacetone via oxidation of glycerol have been established using nano-gold catalysts along with different metal oxide supports such as copper oxide (scheme 4), by the Xu group. It was found that at 80 °C, a pH of 6.7, 10 bar of O<sub>2</sub>, and using copper oxide with the gold catalyst produced high selectivities of 75 % but low yields of only 35 %.<sup>10</sup> Gold as one of the most expensive catalysts restricts the profitability of the research.



**Scheme 4** Gold catalyzed oxidation of glycerol to dihydroxyacetone.<sup>10</sup>

### 1.3.3 Catalytic Oxidation of Glycerol with a Platinum-Bismuth Catalyst

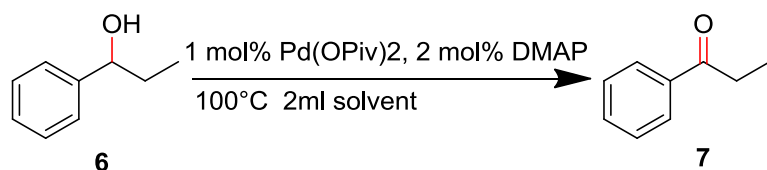
Studies by the Kimura group examined the oxidation of glycerol under mild conditions using a carbon supported platinum – bismuth catalyst (scheme 5). They determined that the platinum-bismuth catalyst was selective for dihydroxyacetone under acidic conditions (pH= 2). Following the group's initial research, other groups determined the optimal catalyst loading of 5 wt% platinum and 5.4 wt% bismuth at 100 °C and 10 bar of O<sub>2</sub> produced 85 % yield.



**Scheme 5** Platinum-bismuth catalyzed oxidation of glycerol to dihydroxyacetone.

### 1.3.4 Catalytic Oxidation with Palladium Catalysts

Previously, research in the Emmert group has established complete oxidation of 1-phenyl-1-propanol **6** to propiophenone **7**, shown in Scheme 6, using catalytic palladium pivalate and pivalic acid as an additive.<sup>11</sup> Results showed that using pyridine ligands such as 4-dimethylaminopyridine, DMAP, 99 % yield of **7** was achieved. These reactions were run under mild conditions at atmospheric pressure using air as an oxidant and toluene as the solvent. Similar results are hoped to be achieved in the reaction of glycerol due to the oxidation of the secondary alcohol.

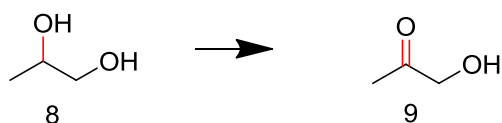


**Scheme 6** Palladium (II) pivalate catalyzed oxidation of 1-phenyl-propanol to propiophenone.

## 1.4 Research

The goal of this research is to investigate the oxidation of glycerol under mild conditions that are safer to humans using non-toxic chemicals and safe manufacturing conditions, for example mild

oxidants such as air and lower pressures of O<sub>2</sub>. Transforming glycerol into a valuable product would encourage the growth of the production of biodiesel with increased profits. This report will be looking at the oxidation of glycerol to dihydroxyacetone shown in Scheme 2 as well as the oxidation of 1,2-propanediol (**8**) to hydroxyacetone (**9**) shown in Scheme 7. **8** will be looked at due to the similarities it has to **4**. The structures are similar except for a missing hydroxyl group.



**Scheme 7** Oxidation of 1,2 propanediol to hydroxyacetone

#### 1.4.1 Significance

The ability to oxidize glycerol under aerobic conditions would reduce the costs in producing dihydroxyacetone from the absence of the extra materials. From past research, using benzoquinone as an oxidant or oxygen at high pressures, high yields were achieved; however this oxidant is not a feasible due to the toxicity of benzoquinone. Subsequently, high pressure oxygen reactions increase the total cost therefore making the system unable to compete with prevailing methods. It is necessary to achieve the yields comparable to those utilizing benzoquinone, but without the safety hazards. The ability to operate at mild conditions would increase the feasibility of production scale-up for dihydroxyacetone. Mild conditions would reduce the costs associated with operating costs and equipment costs and will encourage the increased production of alternative fuels.

#### 1.4.2 Approach

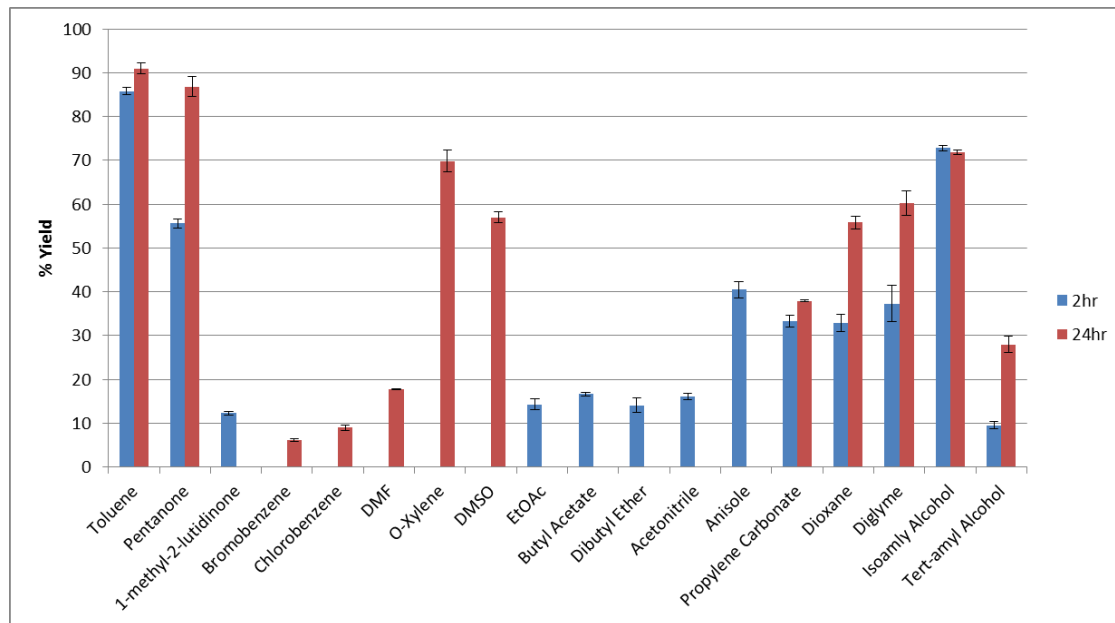
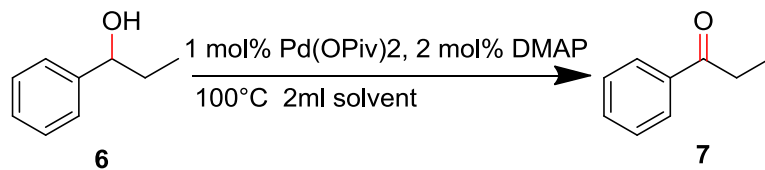
Both glycerol and 1-phenyl-2-propanol contain secondary alcohols. We have already developed a system which can oxidize secondary alcohols, as detailed in the introduction. Therefore, using the complete oxidation of 1-phenyl-2-propanol, depicted in Scheme 6, as a model for the

oxidation of glycerol and hydroxyacetone, is a viable option. We will explore the oxidation of glycerol using both Pd and Ir catalysts and then optimize the conditions for the reaction, including, solvent choice, catalyst concentration, presence and concentration of any additives, etc.

## **2. Results and Discussion**

### **2.1 Solvent System**

We are using the complete oxidation of 1-phenyl-2-propanol, depicted in Scheme 6, as a model reaction. This reaction was optimized to proceed with toluene as the solvent. Glycerol is not soluble in toluene as determined for the previous oxidation of **7**, Scheme 6. Therefore we need to broaden the solvent scope of this reaction. The oxidation of 1-phenyl-2-propanol, depicted in Scheme 6, was used to conduct a solvent screening to explore alternative solvents that would be compatible with the catalyst, palladium pivalate, and give high reaction yields of **7** at 2 and 24 hr time points.



**Figure 4** Solvent screening for the oxidation of 1-phenyl-2-propanol to 1-phenyl-2-propionane

As shown in Figure 4, pentanone gives a yield of 87 % and isoamyl alcohol gives a yield of 72% which makes it a favorable choice of a solvent to be further investigated. Many of the oxygenated solvents (pentanone, DMSO, anisole, propylene carbonate, dioxane) had higher yields for the oxidation of **6** to **7**. It seems that polar solvents (Pentanone, DMSO, Anisole, Propylene Carbonate, Dioxane) are more favorable compared to the nonpolar solvents (Bromobenzene, Chlorobenzene, DMF). Many solvents were not investigated for both 2 hour and 24 hour yields due to cost, safety, or low reactivity. For example,  $\sigma$ -xylene was not further investigated for this study due to the toxicity that it presents to aquatic life and humans.<sup>12</sup> DMSO was not investigated further due to the high cost of the solvent. The most promising solvent choices are pentanone and isoamyl alcohol. During further studies, reactions with **4** in isoamyl alcohol saw that the catalyst was preferentially reacting with the primary alcohol in the solvent rather than the substrate so an alternative solvent was looked into. Tert-amyl alcohol was studied due to its tertiary alcohol

## 2.2 Background Oppenauer Oxidation

The Oppenauer reaction shown in Scheme 8 allows for the selective oxidation of secondary alcohols.<sup>13</sup> The transition metal catalyst reacts in the reversible reaction with the substrate. In the system it is necessary to determine if the catalyst plays a role in the oxidation or if the solvent is being oxidized. Pentanone can undergo this reaction without the presence of catalyst. Pentanone was tested in Scheme 7 without the palladium pivalate catalyst to determine if the Oppenauer oxidation occurs. The results can be seen in Figure 5. With no catalyst pentanone oxidizes **6** to produce **7** with significant yields of 39 % after 24 hr. This disqualifies pentanone as a possible solvent to use in our system. Conversely, in the presence of no catalyst using tert-amyl alcohol as the solvent, less than 2 % yield is achieved (under catalytic conditions, > 25 % yield is observed). Isoamyl alcohol becomes a stronger candidate for the reaction system.

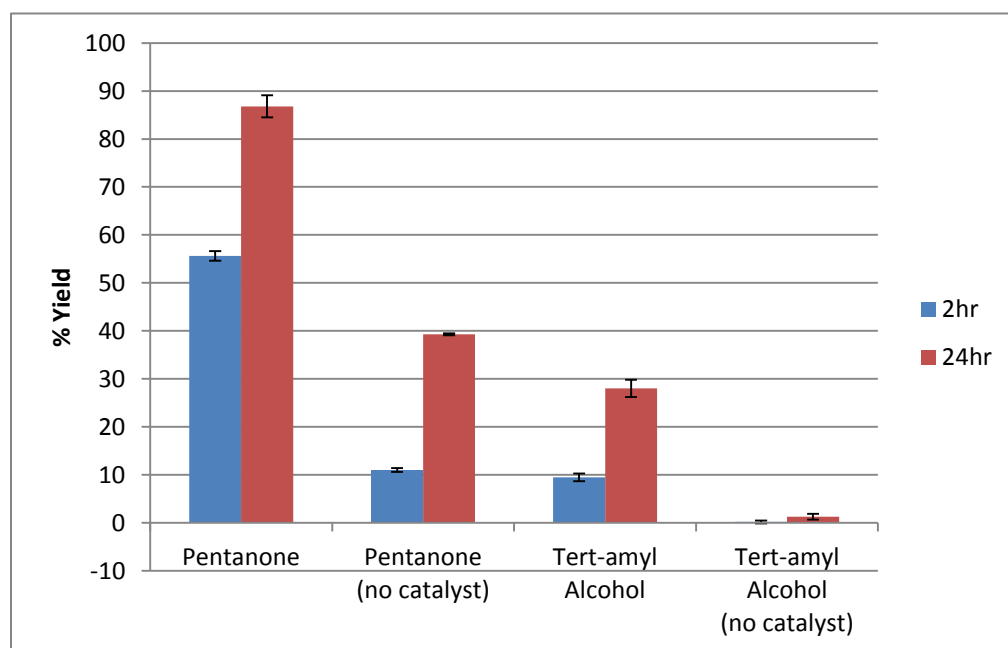
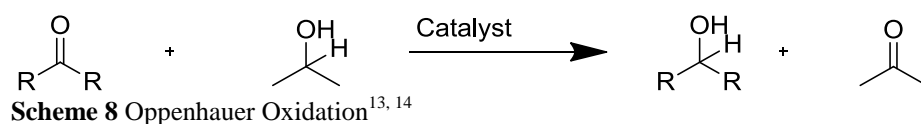
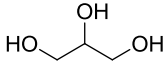
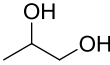

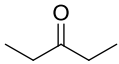

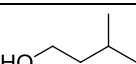
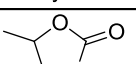
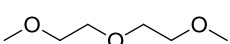

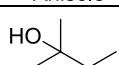


Figure 5 Comparison of oxidation with and without catalyst

## 2.3 Solubility

Due to the viscous nature of glycerol and its polarity, the solubility of glycerol needs to be tested to determine if a homogenous system can be formed. A homogenous system is more beneficial to the catalytic system to increase yields. Glycerol and propylene glycol were dissolved in the most promising solvents determined from the solvent screening to determine the solubility of these compounds at room temperature. The solubility of propylene glycol was explored because glycerol and propylene glycol have similar structures, and there exists a possibility of oxidizing glycerol to hydroxyacetone.

	 <b>Glycerol</b>	 <b>Propylene Glycol</b>
<b>Solvent</b>		
 Toluene	No	No
 3-Pentanone	Slightly	Yes
 1,4-dioxane	Slightly	Yes
 isoamyl alcohol	Yes	Yes
 propylene carbonate	Slightly	Yes
 Diglyme	No	Slightly
 Anisole	No	Yes
 Tert-amyl alcohol	Yes	Yes

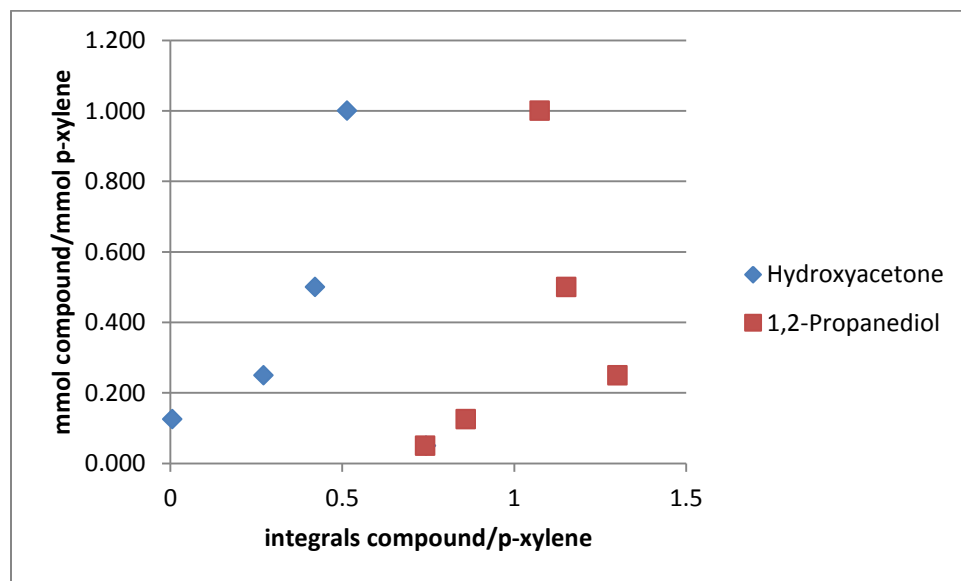
**Table 1** Determination of glycerol and propylene glycol solubility in various solvents

Toluene had the highest product yield of **8** (91 %) observed during the solvent screening however, the insolubilities of both glycerol and propylene glycol deem toluene unsuitable for the oxidation of glycerol or propylene glycol. Pentanone having the second highest yield at 87 % is unsuitable as glycerol is only slightly soluble. Isoamyl alcohol looks to be a promising choice as both glycerol and propylene glycol are soluble and 72 % yield is achieved after 24 hrs for the oxidation of 1-phenyl-2-propanol. Tert-amyl alcohol was tested as the alternative to isoamyl alcohol and proved to be the choice as both glycerol and propylene glycol are soluble in it.

Tert-amyl alcohol was chosen to be the solvent for the system due to its compatibility with the catalyst being able to achieve a

## 2.4 GC Stabilization

To quantify the results of Scheme 2, a reaction was tested on the GC to determine if the compounds were GC stable. The ratio of integrals of the compound versus a known standard of para-xylene was graphed versus the ratio of concentrations. If this relationship of ratios was linear, then these compounds would be deemed GC stable.

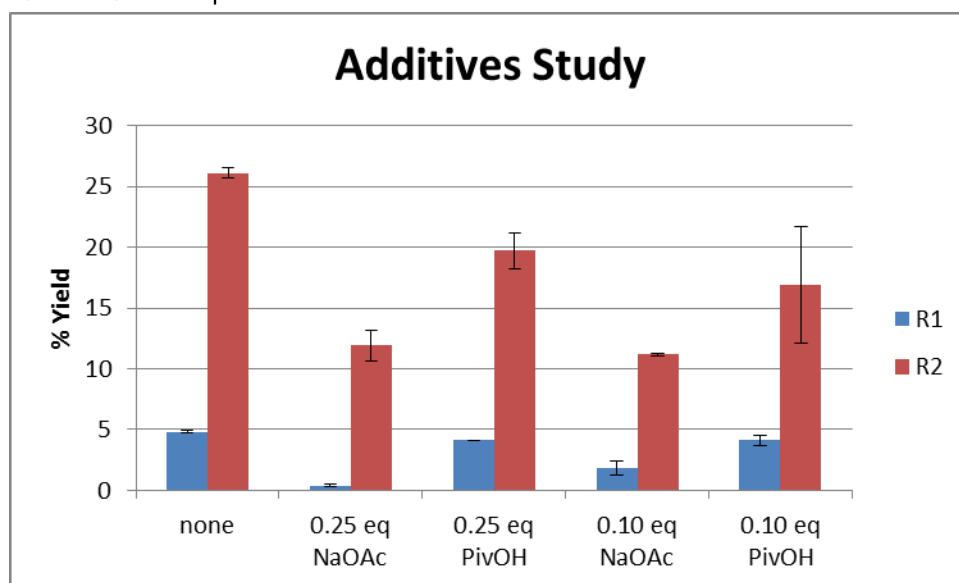
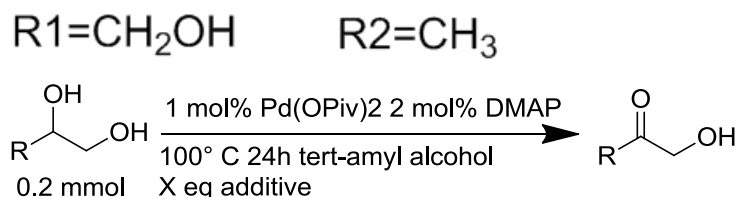


**Figure 6:** GC Stabilization



However, as shown in Figure 6, linear regressions are not observed, therefore the two compounds hydroxyacetone and 1,2-propanediol are not GC stable. For the compounds to be stable the plots would be expected to be linear due to proportional integrals with proportionally increase amounts of compound. Shown in Figure 6, the integral ratios did not proportionally increase with the amounts added so the figure shows undeterminable relations between the amount added and the integral ratios. Without a determinable relation, accurate amounts would not be able to be calculated to calculate the yields of the reaction. NMR spectroscopy was chosen as a better method to quantify the concentration of oxidation products for the remainder of this report.

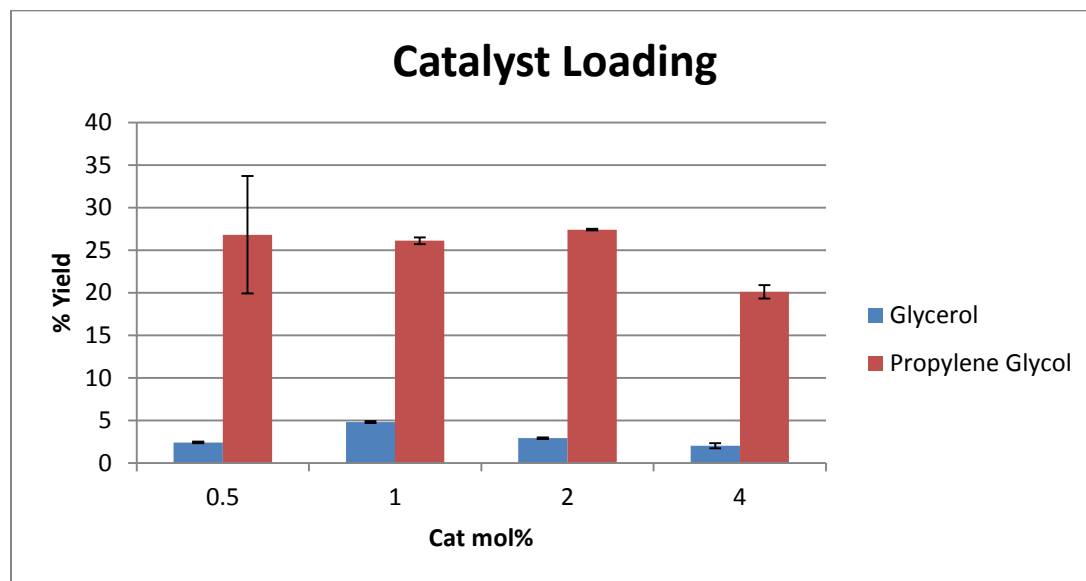
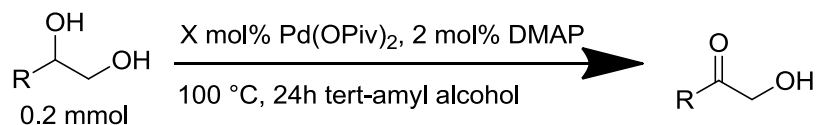
## 2.5 Oxidation Reaction Results



**Figure 7:** Additives Study

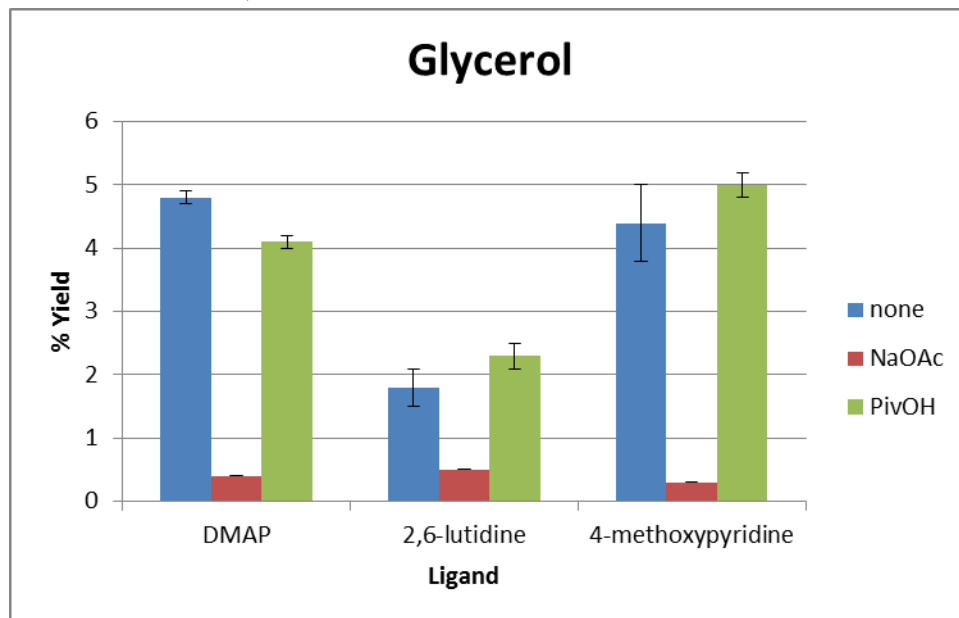
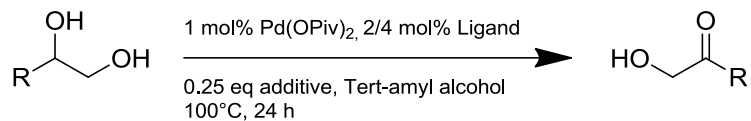
Looking at NaOAc and PivOH as additives for our reaction shows that there is a decrease in yields for both **5** and **9**. Without catalyst, the highest yield achieved for **5** and **9** was 4% and 26% respectively. Using additives to aid our reaction system goes back to the data found previously in our group.<sup>11</sup> The additives in the reaction are supposed to aid in the stabilization of the catalyst,

but these findings contradict what has been previously shown. With the additives, palladium black is still seen in reactions with and without additives. This shows that we are seeing the catalyst being used up without being regenerated back into the catalytic cycle.

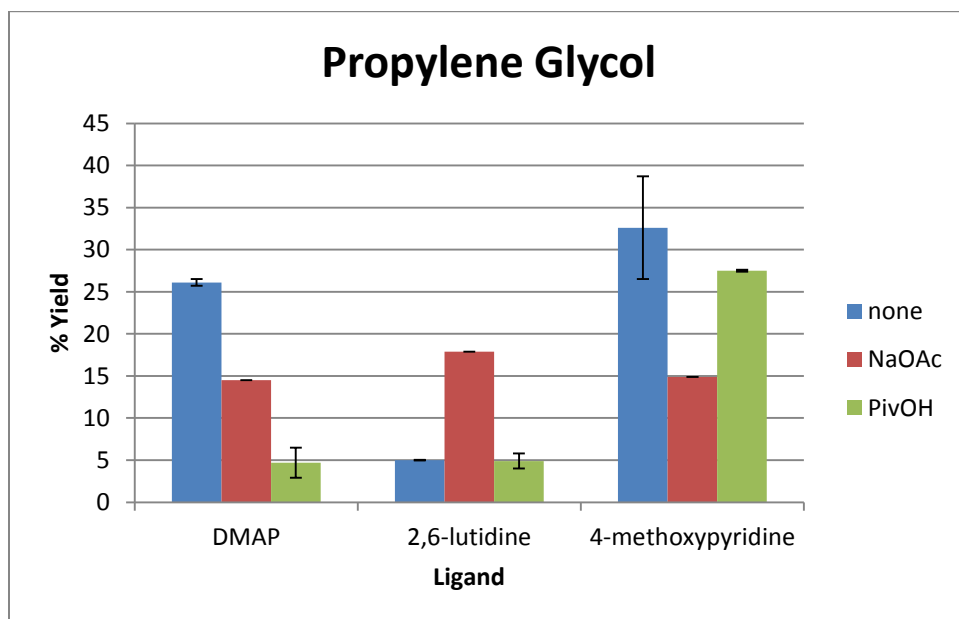


**Figure 8:** Catalyst Loading

Different catalyst loadings were done to analyze the yields with increasing loadings. For both yields of **5** and **9**, there was a relative maximum was seen at 1 mol% and 2 mol% catalyst loading with a 4% yield and 26% yield respectively.



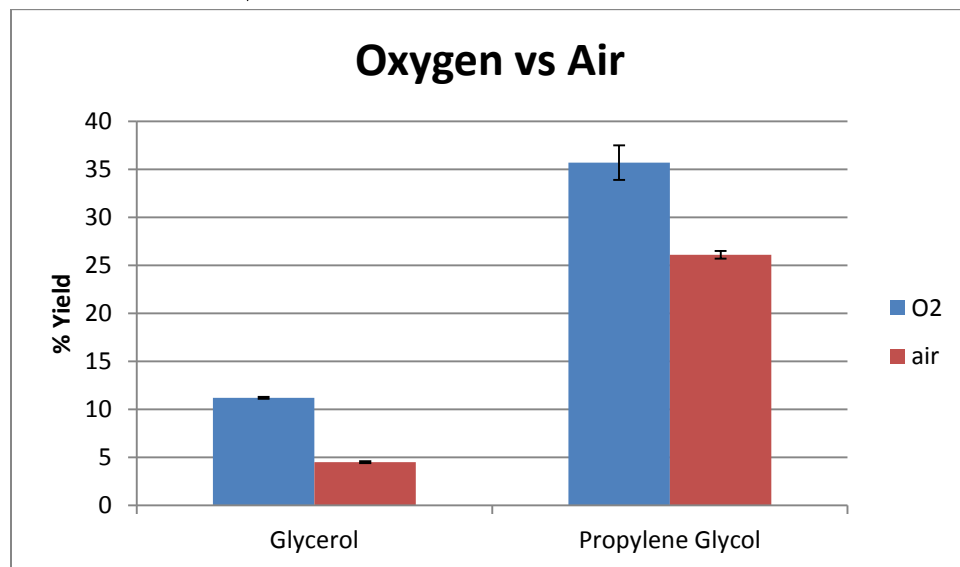
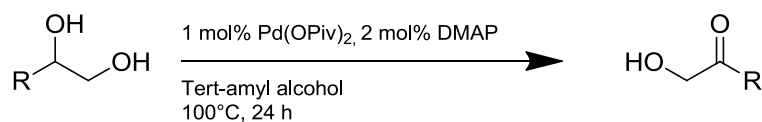
**Figure 9:** Ligand Study for Glycerol Oxidation



**Figure 10:** Ligand Study for Propylene Glycol Oxidation

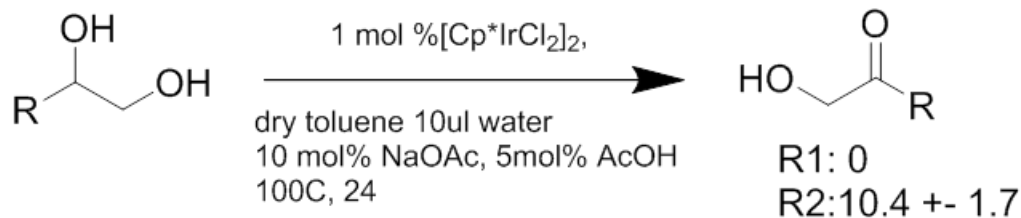
Ligands aid in the catalytic cycle by steric effects that help the catalyst to bind to the substrate. A study was done on the best ligands shown previously done in our group.<sup>11</sup> For both **4** and **8**,

ligands play a substantial role in the yields of the reaction. Depending on the additive used relatively high yields for our system are seen with all three ligands.



**Figure 11:** Oxidation of Substrates in an Oxygen Enriched Environment

These reactions are run under aerobic conditions where oxygen in the air is the oxidant in the reaction. With that in mind, reactions were run under an oxygen enriched environment where it is expected to see reaction yields increase. The results shown in Figure 11 confirm what is to be expected. Yields increase for both **5** and **9** by 7% and 11% respectively. Under oxygen, high yields have been shown by the Xu and Kimura group.<sup>5, 10</sup> Their reactions were done under high pressures of 10 bar. These reactions were done without studying the pressure but were not pressurized to the amount as their groups did. The reactions may not have seen as high yields due to the concentration of oxygen in the solution. At higher pressures, solubility increases, so there would be a higher oxygen concentration in the reaction at higher pressures for their reactions compared to the reactions done. As oxygen is the oxidant for these reactions, higher oxygen concentrations should increase yields as previously shown.



**Scheme 9:** Iridium Catalyst Study

Previously done in our group, the Ir catalyst has shown preferential oxidation for secondary alcohols. Using the Ir catalyst, there was no yield for **5**. For **8**, 10.4% yield was found.

### 3. Conclusion

The oxidation of glycerol and 1,2-propanediol was able to yield a maximum of 11% and 36% respectively. For both reactions, the maximums were found at 1 mol% Pd(OPiv)<sub>2</sub>, 2 mol% DMAP, and 100 °C for 24h in an oxygen enriched environment. It was found that ligands play an important role in the yields of the reactions with the catalyst as previously shown by our group. The role of additives contradicts what was previously known for our catalyst as the yields decreased with the additives.

### 4. Future Directions

The results show that the reactions can be completed under mild reaction conditions. Higher yields need to be achieved in order for this reaction system to be comparable to the reaction systems completed by previous groups. This can be achieved by looking to further optimize the reaction system. Other additives and different ligands can be looked at to optimize conditions to provide the highest yield. Further studying the effects of pressure with oxygen could further increase the yields due to the solubility of oxygen. The reaction system needs to be improved before it can be scaled up for use in industry.

## 5. Experimental

### 5.1 Solvent System Procedure

The reactions were done following the procedure developed by John, L et. al.<sup>11</sup> A 20 mL scintillation vial with a Teflon coated stirbar was used as the reaction vessel for all experiments. A standard stock solution of 100  $\mu\text{L}$   $\text{Pd}(\text{OPiv})_2$  (6.18 mg dissolved to 2 mL of solvent to make a 0.2 M solution), a standard stock solution of 100  $\mu\text{L}$  4-dimethylaminopyridine (DMAP) (9.77 mg dissolved to 2 mL of solvent to make a 0.04 M solution), and a standard stock solution of 400  $\mu\text{mol}$  1-phenyl-1-propanol (**1**) (0.675 mL was diluted to 10 mL of solvent to make a 0.5M solution) were each added to the vial. The stock solutions were made with the solvent used for each experiment. The solution was then diluted to a final volume of 2.0 mL of the solvent. The vial was capped with a Teflon-lined cap. The vial was heated to 100  $^\circ\text{C}$  stirred continuously on a hot plate for the duration of the experiment. After completion and cooled to room temperature, 10  $\mu\text{L}$  of para-xylene was added to the solution. The reaction solution was then analyzed via GC. Each reaction was completed in triplicate.

### 5.2 Reaction Study Procedure

A 20 mL scintillation vial was used with a Teflon coated stirbar for all reactions. A standard stock solution of 400  $\mu\text{L}$  of the substrate, either glycerol (460.5 mg dissolved to 10 mL to make a 0.5 M solution for 0.2 mmol) or 1,2-propanediol, (380.5 mg dissolved to 10 mL to make a 0.5M solution for 0.2 mmol), and a standard stock solution of  $\text{Pd}(\text{OPiv})_2$  of varying concentrations, see results. NaOAc was measured and added by weight to the vial if the reaction called for it. A standard stock solution of 100  $\mu\text{L}$  of the additive pivalic acid (102.1 mg dissolved to 2 mL to make a 0.5 M solution for 0.05 mmol) was added to reaction that called for it.

For experiments being run under  $\text{O}_2$ , 20 mL pressure relief reaction vials were used.  $\text{O}_2$  was bubbled through the reaction for 2 minutes. The vials were placed on a hot plate and heated to 100  $^\circ\text{C}$  for two hours. After the time had elapsed, the vials were cooled to room temperature and 10  $\mu\text{L}$  of 1,1,2-trichloroethane was added as an internal standard. 100  $\mu\text{L}$  of the sample was added to 400  $\mu\text{L}$  CDCL and the solutions were analyzed on NMR. Concentration was

determined by integration of the 4.3 ppm shift in dha, the 4.2 ppm shift in HA, and the 5.7 ppm shift in 1,1,2-trichloroethane.

The reactions looking at the affects can be seen in Tables 2 & 3 testing the best ligands found in previous work done by the group. The effects of catalyst loading can be seen in Tables 4 & 5. Due to the decreased yields with additives, reactions were tested at lower additive loadings can be seen in Tables 6 & 7. Oxygen enriched environments were tested to investigate the yields under higher oxygen environments seen in Tables 8 & 9.

Glycerol Ligand Study				
1 mol% Pd(Opiv) <sub>2</sub> , 100°C, tert-amyl alcohol, 24h, 0.25 eq additive				
Ligand	mol %	additive	% Yield	Std Dev
DMAP	2	none	4.8	0.1
		NaOac	0.4	0.1
		PivOH	4.1	0.01
2,6-lutidine	4	none	1.8	0.3
		NaOac	0.5	0.02
		PivOH	2.3	0.2
4-methoxypyridine	4	none	4.4	0.6
		NaOac	0.3	0.02
		PivOH	5	0.2

**Table 2:** Glycerol Ligand Study

1,2-Propanediol Ligand Study				
1 mol% Pd(Opiv) <sub>2</sub> , 100°C, tert-amyl alcohol, 24h, 0.25 eq additive				
Ligand	mol %	additive	% Yield	Std Dev
DMAP	2	none	26.1	0.4
		NaOac	11.9	1.3
		PivOH	19.7	1.5
2,6-lutidine	4	none	5	0.02
		NaOac	17.9	0.3
		PivOH	4.9	0.9
4-methoxypyridine	4	none	32.6	6.1
		NaOac	14.9	0.8
		PivOH	27.5	0.1

**Table 3:** 1,2-Propanediol Ligand Study

Glycerol Catalyst Loading				
X mol% Pd(OPiv) <sub>2</sub> , 2X mol% DMAP, tert-amyl alcohol, 100°C				
mol % Pd(OPiv) <sub>2</sub>	Yield 2h	Std Dev	% Yield 24h	Std Dev
0.5	2.6	0.1	3.1	
1	4.5	0.1	4.8	0.1
2	2.3		2.9	0.1
4	2.2	0.1	2	0.3

**Table 4:** Glycerol Catalyst Loading

1,2 Propanediol Catalyst Loading				
X mol% Pd(OPiv) <sub>2</sub> , 2X mol% DMAP, tert-amyl alcohol, 100°C				
mol % Pd(OPiv) <sub>2</sub>	Yield 2h	Std Dev	% Yield 24h	Std Dev
0.5	15.5	0.2	26.8	6.9
1	26.1	0.4	26.1	0.4
2	27.8	2.4	27.4	0.1
4	2.9	0.5	20.1	0.8

**Table 5:** 1,2-Propanediol Catalyst Loading

Glycerol Additive Loading			
1 mol% Pd(OPiv) <sub>2</sub> , 2mol% DMAP, tert-amyl alcohol, 100°C, 24h			
Additive		% Yield	Std Dev
none		4.8	0.1
NaOAc	0.25 eq	0.4	0.1
	0.1 eq	1.9	0.6
PivOH	0.25 eq	4.1	0.01
	0.1 eq	4.1	0.4

**Table 6:** Glycerol Additive Loading

1,2-Propanediol Additive Loading			
1 mol% Pd(OPiv) <sub>2</sub> , 2mol% DMAP, tert-amyl alcohol, 100°C, 24h			
Additive		% Yield	Std Dev
none		26.1	0.4
NaOAc	0.25 eq	11.9	1.3
	0.1 eq	11.2	0.1
PivOH	0.25 eq	19.7	1.5
	0.1 eq	16.9	4.8

**Table 7:** 1,2-Propanediol Additive Loading



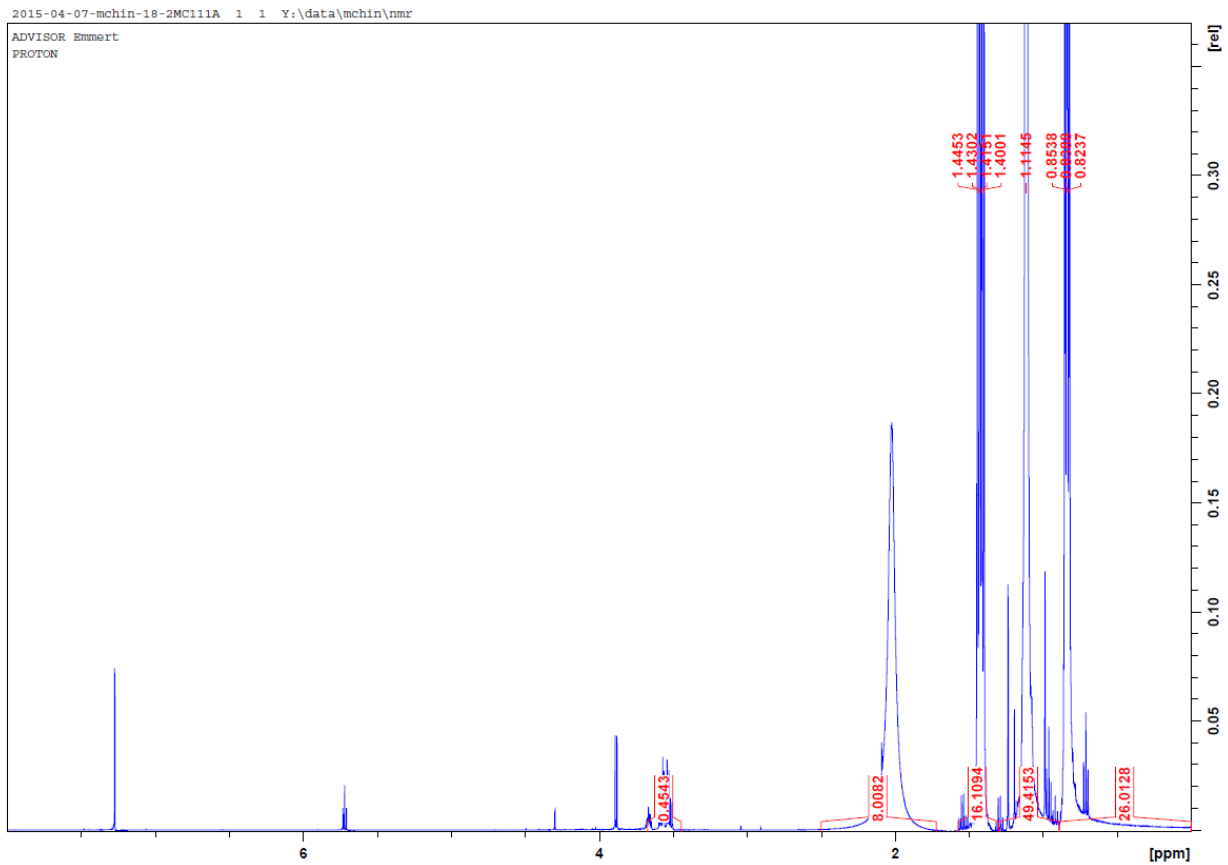
Glycerol Oxygen Study					
1 mol% Pd(OPiv)2, 2mol% DMAP, tert-amyl alcohol, 0.25eq additive 100°C					
Oxidant	Additive	% Yield 2h	Std Dev	% Yield 24h	Std Dev
air	none	4.5	0.1	4.8	0.1
	PivOH	1.8	0.1	4.1	0.01
O2	none	11.2	0.1	8.8	1
	PivOH	2.9	0.2	4.2	1

**Table 8:** Glycerol Oxygen Study

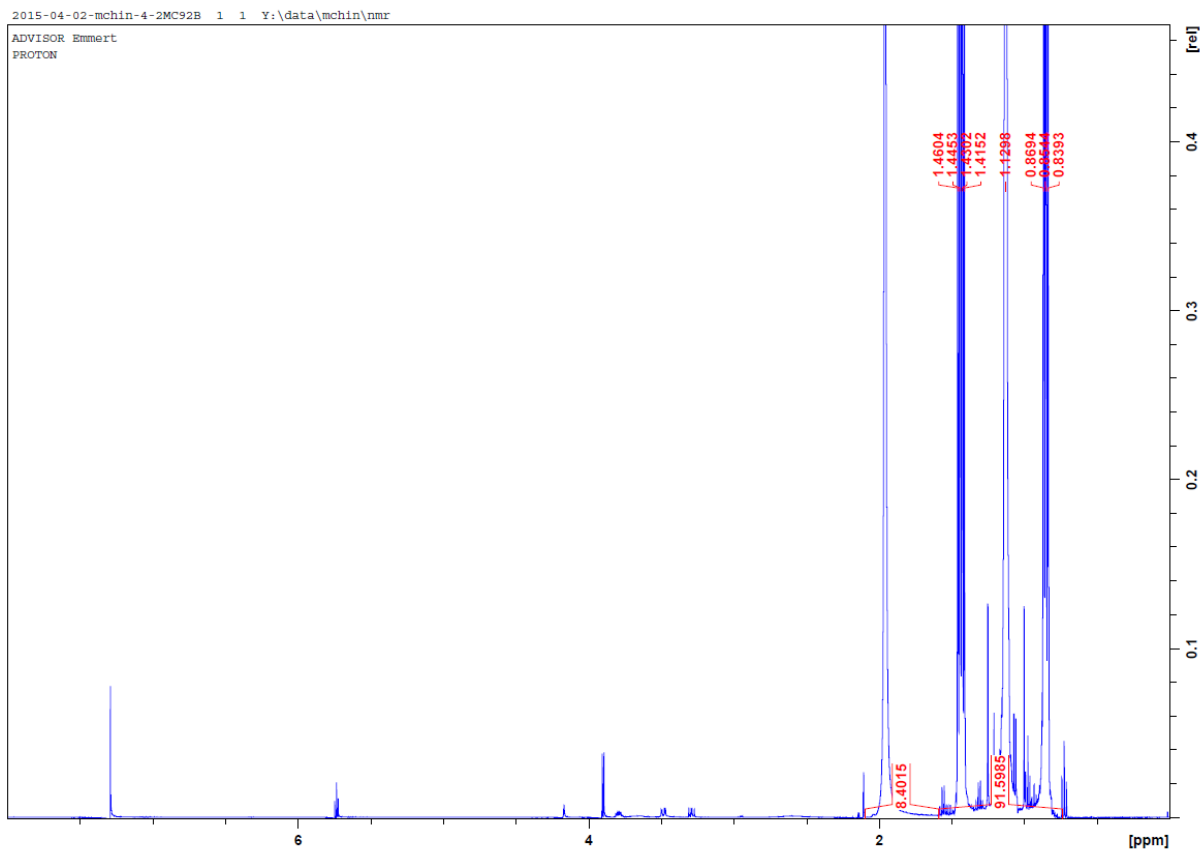
1,2-Propanediol Oxygen Study					
1 mol% Pd(OPiv)2, 2mol% DMAP, tert-amyl alcohol, 0.25eq additive 100°C					
Oxidant	Additive	% Yield 2h	Std Dev	% Yield 24h	Std Dev
air	none	26.5	7.6	26.1	0.4
	PivOH	4.7	1.8	11.9	1.3
O2	none	35.7	1.6	32.5	2.8
	PivOH	10.3	1.7	18.3	1.1

**Table 9:** 1,2-Propanediol Oxygen Study

## 5.3 NMR



**Figure 12:** NMR of Oxidation of Glycerol to Dihydroxyacetone



**Figure 13:** NMR of Oxidation of 1,2-Propanediol to Hydroxyacetone

Shown in Figure 12 is the NMR of the oxidation of **4** to **5**. To calculate the yields the proportions between the peaks for **4** and the internal standard 1,1,2-trichloroethane can be used to calculate the amount product of **5** due to a known amount of standard being added. The singlet peak at 4.3 ppm is used for **5** and the triplet peak at 5.7 ppm is used to calculate the yields. The same can be done for **9**. Shown in Figure 13 is the NMR of the oxidation of **8** to **9**. Using the peak at 4.2 ppm for **9**, the yield can be calculated similar to **5**.

## 6. References

1. Shafiee, S.; Topal, E., When will fossil fuel reserves be diminished? *Energy policy* **2009**, *37* (1), 181-189.
2. U.S. Energy Consumption from 1950-2011. Administration, U. S. E. I., Ed.
3. Soleki, M.; Anna, S.; Epstein, B., Advanced Biofuel Market Report 2013. San Francisco, 2013.
4. Díaz-Álvarez, A. E.; Cadierno, V., Glycerol: A promising Green Solvent and Reducing Agent for Metal-Catalyzed Transfer Hydrogenation Reactions and Nanoparticles Formation. *Applied Sciences* **2013**, *3* (1), 55-69.
5. Katryniok, B.; Kimura, H.; Skrzyńska, E.; Girardon, J.-S.; Fongarland, P.; Capron, M.; Ducoulombier, R.; Mimura, N.; Paul, S.; Dumeignil, F., Selective catalytic oxidation of glycerol: perspectives for high value chemicals. *Green Chemistry* **2011**, *13* (8), 1960-1979.
6. Barbirato, F.; Himmi, E. H.; Conte, T.; Bories, A., 1, 3-Propanediol production by fermentation: an interesting way to valorize glycerin from the ester and ethanol industries. *Industrial Crops and Products* **1998**, *7* (2), 281-289.
7. Painter, R. M.; Pearson, D. M.; Waymouth, R. M., Selective catalytic oxidation of glycerol to dihydroxyacetone. *Angewandte Chemie International Edition* **2010**, *49* (49), 9456-9459.
8. Chung, K.; Banik, S. M.; De Crisci, A. G.; Pearson, D. M.; Blake, T. R.; Olsson, J. V.; Ingram, A. J.; Zare, R. N.; Waymouth, R. M., Chemoselective Pd-Catalyzed Oxidation of Polyols: Synthetic Scope and Mechanistic Studies. *Journal of the American Chemical Society* **2013**, *135* (20), 7593-7602.
9. Bedner, M.; MacCrehan, W. A., Transformation of acetaminophen by chlorination produces the toxicants 1, 4-benzoquinone and N-acetyl-p-benzoquinone imine. *Environmental science & technology* **2006**, *40* (2), 516-522.
10. Liu, S.-S.; Sun, K.-Q.; Xu, B.-Q., Specific Selectivity of Au-catalyzed Oxidation of Glycerol and Other C3-polyols in Water without the Presence of a Base. *ACS Catalysis* **2014**.
11. John, L. C.; Gunay, A.; Wood, A. J.; Emmert, M. H., Catalysts for convenient aerobic alcohol oxidations in air: systematic ligand studies in Pd/pyridine systems. *Tetrahedron* **2013**, *69* (27), 5758-5764.
12. Kandyala, R.; Raghavendra, S. P. C.; Rajasekharan, S. T., Xylene: An overview of its health hazards and preventive measures. *Journal of oral and maxillofacial pathology: JOMFP* **2010**, *14* (1), 1.
13. Graves, C. R.; Zeng, B.-S.; Nguyen, S. T., Efficient and selective Al-catalyzed alcohol oxidation via Oppenauer chemistry. *Journal of the American Chemical Society* **2006**, *128* (39), 12596-12597.
14. Bäckvall, J.-E., Transition metal hydrides as active intermediates in hydrogen transfer reactions. *Journal of organometallic chemistry* **2002**, *652* (1), 105-111.