APPLICATION OF METAL CATALYSTS FOR HIGH SELECTIVITY OF GLYCEROL CONVERSION TO ALCOHOLS

Final Report

KLK758

N10-10

National Institute for Advanced Transportation Technology

University of Idaho

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November 2010

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Application of Metal Catalysts for High Selectivity of Glycerol Conversion to Alcohols		5. Report Date November 2010	
		6. Performing Organization Code KLK758	
7. Author(s) He, B. Brian		8. Performing Organization Report No. N10-10	
9. Performing Organization Name and Address National Institute for Advanced Transportation Technology University of Idaho PO Box 440901; 115 Engineering Physics Building Moscow, ID 83844-0901		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No. DTRT07-G-0056	
12. Sponsoring Agency Name and Address US Department of Transportation Research and Special Programs Administration 400 7th Street SW Washington, DC 20509-0001		13. Type of Report and Period Covered Final Report: 08/2009 – 10/2010	
		14. Sponsoring Agency Code USDOT/RSPA/DIR-1	
15. Supplementary Notes:			

16. Abstract

The objective of this project is to determine the applicability of metal-based catalysts and optimize the process conditions for thermochemically producing primary alcohols. Metal catalysts were evaluated for their selectivities for producing alcohols, specifically methanol, ethanol, and propanol. Raney nickel catalyst showed the best activity and application of Raney catalysts greatly improved the selectivity towards alcohols. Water was found to be significant in the catalytic thermochemical conversion of glycerol to alcohols. Additionally, water inhibited tar formation thus improved the product yields.

Reaction temperature, reaction time, application rate of catalysts, and initial water to glycerol ratio (WTGR) were identified as the most important process parameters. Ethanol production increased at extended reaction time and increased WTGR. It was also influenced by the catalyst application rate in a linear relationship. However, adding catalyst higher than 7%wt did not further improve the productivity. Meanwhile, methanol formation was only significantly affected by the initial composition of the reactants and the operating temperature in both batch and fed-batch experiments. The optimum condition for producing ethanol was found to be at 1.82 WTGR and 223 °C for 45 min of reaction and using 10%wt of Raney nickel catalyst. The highest yield of ethanol at this condition was 11.37 %mol.

17. Key Words Crude glycerol, biodiesel, thermochemical conversion		18. Distribution Statement Unrestricted; Document is available to the public through the National Technical Information Service; Springfield, VT.		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 25	22. Price …	

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EXECUTIVE SUMMARY

Converting the surplus, low quality glycerol (a byproduct from biodiesel production) to primary alcohol remains a hot topic in both the industry and research communities. Results from our previous research entitled, "Thermal Processing of Low-grade Glycerol to Alcohols for Biodiesel Production," showed methanol, ethanol, and propanol can be produced from crude glycerol in biodiesel production. Improving the efficiency of the conversion process becomes a logical next step. Metal-based catalysts have been proven effective in increasing the selectivity and productivity of targeted products in similar processes. This project aimed to determine the applicability of metal-based catalysts and optimize the corresponding process conditions for producing primary alcohols with high selectivity from the glycerol in biodiesel production. This paper reports the activities conducted and the results of the project entitled "Application of Metal Catalysts for High Selectivity of Glycerol Conversion to Alcohols."

Commercially available catalysts specifically Raney nickel, copper reforming HiFuel R120 catalyst, iron-chrome HiFuel W210 catalyst, and Pt/C catalyst were purchased and tested. These catalysts were selected because of its capability in cleaving carbon-to-carbon or carbon-to-oxygen bonds in hydrocarbons. In theory, breaking these types of bonds in glycerol can produce methanol and ethanol. Due to the variation on the application of the catalysts purchased, each catalyst was investigated at a wide range of operating conditions to broadly examine the catalyst's capability to produce alcohols. Results of the preliminary tests showed that nickel catalysts exhibited the best activity towards the production of alcohols specifically ethanol. It also confirmed that the application of metal catalysts to thermochemical processing of glycerol improves its alcohol selectivity and energy efficiency.

Using the results from the preliminary investigation, experiments were designed to investigate the effects of the major process parameters on the production of alcohols. Reaction time, reaction temperature, the ratio of water and glycerol in the feed, mass of catalyst, and reducing gas were identified as the possible major process parameters. Three sets of experiments were designed and used in this research project to investigate the effects of these parameters. The first set of experiments examined the effect of reaction time, initial amount of water, and mass of catalysts applied in the absence of a reducing gas. Carbon monoxide gas was used in the second set of

experiments to determine the effect of reducing gases to alcohol production. In the last set of experiments, a feeder was used to obtain solid conclusions on the effects of reaction temperature.

In addition to the investigation of the effects of the parameters, various combinations of nickel, platinum, and different supports were also purchased, made, and tested. This was conducted to find the best possible catalyst for the thermochemical conversion of glycerol to methanol and ethanol. Nickel and platinum catalysts with different supports, e.g., carbon and alumina, were purchased and tested. Customized catalysts, such as nickel on cerium oxide and nickel on zeolite, were also made in the laboratory and tested in the search of the best catalyst.

Results of the experiments showed that ethanol production increases at longer reaction time and higher water to glycerol ratios. It was also influenced by the amount of catalyst in which a direct linear relationship was observed from up to seven grams of catalysts. However, adding more catalyst did not improve the productivity of the process towards alcohols. It was hypothesized that the amount of catalysts suspended in the solution had reached its limitation. On the other hand, methanol formation was only significantly affected by the initial amount of water in the reactant. In the case of reaction temperature, the results of the experiments for both with and without the feeder suggested that reaction temperature influences the amount of alcohols produced in the process. In the search for the most active catalyst, it was found that Raney nickel had the highest activity in terms of selectivity in producing ethanol and conversion of glycerol to products. Using Raney nickel catalyst, the results in the process optimization showed that up to 11.37 %mol of ethanol can be produced. The optimum conditions in producing ethanol was found to be 1.82 WTGMR and 223 °C for 45 min of reaction and using 10 g of Raney nickel catalyst per 100 g of solution. In order to further improve the alcohol yield of the process, a study on reactive distillation or continuous reactor systems are recommended for future research.
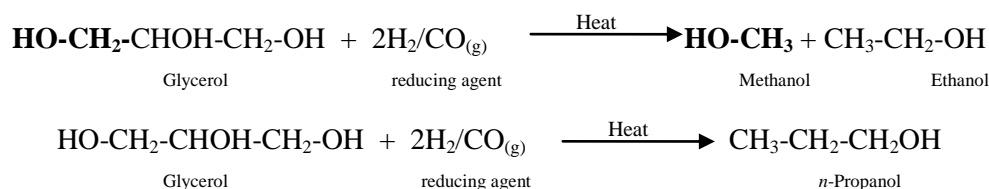
DESCRIPTION OF PROBLEM

Background

Glycerol, also named glycerin, a polyhydric alcohol, is the major byproduct of biodiesel production. The exponential expansion of the biodiesel industry in recent years has produced large quantity of low-quality glycerol. In 2008, approximately 500 million lbs of this low quality byproduct from biodiesel industry was produced. This surplus of glycerol has flooded its market as a raw industrial material and resulted in a consequent drop in glycerol value. With this diminishing value and increasing surplus of crude glycerin, the economic competitiveness of biodiesel against other energy sources will definitely struggle. A technology to convert glycerol to valuable products is needed to make the biodiesel industry more competitive and sustainable.

Thermochemical conversion of glycerol to monohydric alcohols is a process to potentially increase the value of glycerin. Thermochemical conversion uses heat to breakdown compounds into simpler compounds. Monohydric alcohols are organic compounds that have only one hydroxyl group. Glycerin, on the other hand, is a three carbon compound with each carbon containing a hydroxyl group. Breaking the carbon-to-carbon bonds or removing some of the hydroxyl groups in the glycerol will produce monohydric alcohols. Methanol, the simplest among these alcohols, produced from glycerol can be used as a reactant in the production of biodiesel from triglycerides. Meanwhile, ethanol and propanol are considered good substitutes to gasoline. In Brazil, 70% of their transportation energy comes from ethanol. In the United States, many states have mandated the blending of ethanol in gas sold at pumps.

The results from our previous research project entitled "Thermal Processing of Low-grade Glycerol to Alcohols for Biodiesel Production," funded by NIATT, showed that glycerol decomposes and converts to monohydric alcohols at temperatures above 300°C with the presence of a reducing agent (hydrogen or carbon monoxide). Meanwhile, other products including formaldehydes and acetaldehydes are also produced. The possibility of acrolein formation in such a reaction environment likewise poses a concern (Buhler et al., 2002). The percentage of the targeted monohydric alcohols produced was low even if there was a high percentage of glycerol that had been converted. We are currently working on improving the conversion efficiency to the desired products by exploring the optimum operating conditions for the process. One possible

reason for the inefficiency in producing monohydric alcohols is that side reactions such as conversion to other chemicals and char may have been favored. The challenge is to find ways to direct the reactions during thermochemical conversion towards producing monohydric alcohols. In other similar processes, such as converting glycerol to ethylene glycol selectively, ruthenium-based catalysts were employed (Alhanash and Kozhevnikov, 2008). The same principles behind these processes can be employed in producing methanol, ethanol, and propanol or their mixture from glycerol.

Conventional thermochemical conversions involve high energy requiring operating conditions, such as high temperature, in order to break chemical bonds which also favor further decomposition of the desired products to unwanted compounds like char. Catalysts have the capability to decrease the energy required to break chemical bonds by lowering the activation energy of a reaction. Another important role that catalysts play is its selectivity of breaking chemical bonds in order to produce the desired products. For glycerol to be converted to methanol and/or ethanol, the carbon-to-carbon bonds and one carbon-to-oxygen bond will have to be broken and extra oxygen be removed selectively. Breaking down two of the three carbon-to-oxygen bonds will lead to propanol as shown in the reactions below.

$$\textbf{HO-CH}_2\text{-CHOH-CH}_2\text{-OH} \; + \; 2H_2/CO_{(g)} \quad \xrightarrow{\text{Heat}} \quad \textbf{HO-CH}_3 + CH_3\text{-CH}_2\text{-OH}$$

Glycerol   reducing agent   Methanol   Ethanol

$$HO\text{-}CH_2\text{-CHOH-CH}_2\text{-OH} \; + \; 2H_2/CO_{(g)} \quad \xrightarrow{\text{Heat}} \quad CH_3\text{-CH}_2\text{-CH}_2OH$$

Glycerol   reducing agent   *n*-Propanol

The proposed reactions involve similar chemical reactions used in large-scale industrial processes like cracking (breaking of long-chain compounds into shorter compounds), dehydration (removal of oxygen and hydrogen molecules from the compound), and hydrogenation (addition of hydrogen to a compound). These processes are inefficient in the absence of a catalyst and industries have used catalysts, specifically metal-based catalysts, for more profitable large-scale production. Metal-based catalysts contain metals or metal oxides which adsorb the reactants where the reaction takes place. These metals can be used in pure form but typically it is bonded to organic or inorganic supports for the ease of recovery of the catalyst. For high temperature processes, inorganic supports are preferred over organic supports since

they are thermally stable and have reasonable heat transfer capabilities (Hartley, 1985). There is a wide range of metals, metal oxides, and inorganic supports that are used in large-scale industrial processes. Some examples are copper, nickel, and platinum which are used in hydrogenation of acetone to propanol; palladium supported on zeolite which is used in paraffin hydrocracking; and rhenium and platinum on aluminum oxide support used in paraffin dehydrogenation (Kroschwitz and Howe-Grant, 1991). Most of the developed industrial metal-based catalysts have been proven to be efficient in the conversion of hydrocarbons and some organic compounds to valuable products. They can also possibly be utilized in the hydrogenation, dehydration, and/or cracking of glycerol in its conversion to value-added products.

A study reports a successful conversion of glycerol to propylene glycol, a three-carbon compound with two hydroxyl groups, using commercially available metal catalysts and hydrogen as the reducing agent (Dasari et al., 2005). Nickel, copper, and platinum-based catalysts were tested, and the results showed that the reaction selectivity in producing propylene glycol was up to 64.5%. Moreover, the process was able to remove one hydroxyl group from glycerol even at moderate temperature conditions (200°C). This supports our observation that catalysts significantly decreased the activation energy of reactions. Without catalysts, glycerol would hardly decompose or react with a reducing agent at temperatures lower than 280°C. Meanwhile, metal catalysts aid the breaking of carbon-to-carbon bonds in glycerol as shown in another study on steam reforming of glycerol (Slinn et al., 2008). We believe that metal-based catalysts will also assist and selectively break the bonds in the glycerol as discussed earlier to produce methanol, ethanol, and propanol or their mixture.

Objective

The specific goal of this project is to determine the applicability of metal-based catalysts for thermochemically producing primary alcohols from the waste glycerol derived from biodiesel production and optimize the corresponding process conditions for high selectivity of glycerol conversion to alcohols. The purpose of this report is to provide a summary of the research project and the results gathered from the tasks conducted.

METHODOLOGY AND RESULTS

Screening and Testing of Commercially Available Catalysts

Studies have given evidence that metal-based catalysts such as copper, platinum, nickel, and iron can be used in converting glycerol to other compounds. However, product selectivity and effectiveness of a catalyst depends on the type of metal used and the structure of support. For example, nickel based metals have been used in hydrogenation of unsaturated hydrocarbons, aldehydes, and ketones; while copper based metals have been found to favor dehydrogenation of glycerol to hydroxyacetone (Kroschwitz and Grant, 1991; Sato et. al., 2008). On the other hand, zeolites, a type of inorganic support for metal catalysts, have been used to promote catalytic cracking. Therefore, it was essential to conduct preliminary research on different kinds of metal-based catalysts.

Experiments were designed and conducted using the 300 mL PARR 4560 Pressure Reactor System available at the Biofuels Research Laboratory in the Department of Biological and Agricultural Engineering (BAE) at the University of Idaho. The reactor system has been established and used for previous research on thermochemical conversion of glycerol to products. Commercial catalysts for reforming and hydrogenation were purchased and tested. Catalysts with copper, iron, platinum, and nickel metals were considered in this research. The commercial catalysts used in the study were Raney nickel (purchased from Sigma-Aldrich), copper reforming HiFuel R120 catalyst (from Alfa Aesar), iron-chrome HiFuel W210 catalyst (from Alfa Aesar), and Pt/C catalyst (from Alfa Aesar). These catalysts were selected since they have been used in cleaving carbon-to-carbon or carbon-to-oxygen bonds in hydrocarbons. The amount of alcohols in the liquid product was determined using GC-FID.

The catalysts purchased were designed for different applications. For example, Raney nickel is effective for hydrogenation of compounds; while copper reforming HiFuel R120 catalysts is used for reforming methanol. Thus, each catalyst was investigated at a wide range of operating conditions to broadly examine the catalyst's capability to produce alcohols. During the preliminary testing, great amounts of data were gathered but not all of the runs yielded to alcohols nor converted glycerol to products. Table 1 summarizes a portion of the results of the preliminary investigation of the catalysts and their corresponding alcohol yields. In all of these

treatments, a batch system was used. For treatments 1 to 4 where pure glycerol was used, tar was produced which caused the deactivation of the catalysts. It was hypothesized that the temperature was not uniform throughout the solution and tar formed in the hot spots. In the case of copper reforming HiFuel R120 catalyst, the liquid product was not analyzed because white precipitate formed during preparation for the analysis. The white precipitate is believed to have been caused by the presence of copper ions in the sample that reacted with the acetone-water solvent. The presence of copper ions in the solution was supported by the destruction of the catalyst during the reaction. In a separate experiment, the catalyst did not melt when treated at 300°C and 400°C in a muffle furnace for two hours. With this, it was hypothesized that the catalyst support was not able to withstand the high pressure conditions of the reaction.

Table 1: Preliminary Results of Metal Catalyst Effects on Alcohol Production

Treatment	Parameters					Alcohol in liquid product (%wt)			
	T (°C)	RT (min)	Catalyst	WTGR	Reducing gas	MeOH	2-P	EtOH	1-P
1	330	120	Nickel	NW	H_2 (at 400 psi)	1.319	ND	ND	1.71
2	330	120	Iron	NW	H_2 (at 400 psi)	0.323	ND	ND	0.484
3	330	120	Copper	NW	H_2 (at 400 psi)	NA	NA	NA	NA
4	200	120	Copper	NW	H_2 (at 400 psi)	NA	NA	NA	NA
5	200	90	Nickel	1:1	H_2 (at 300 psi)	0.369	ND	0.972	0.085
6	230	45	Nickel	1:1	H_2 (at 300 psi)	0.539	ND	2.796	0.204
7	230	90	Platinum	1:1	H_2 (at 300 psi)	ND	ND	ND	ND
8	230	45	Nickel	1:1	No gas	0.574	0.297	2.854	0.173
9	230	45	Iron	7:3	No gas	ND	ND	ND	ND
10	300	45	Platinum	1:1	No gas	0.507	0.055	1.174	0.677

Legends: NW – no water added in the reactor NA – sample was not analyzed due to presence of precipitates
T – reaction temperature RT – reaction time
ND- not detected 1-P – n-propanol 2-P – isopropanol
EtOH – ethanol MeOH – methanol
WTGR – Water to Glycerol Mass Ratio

The results from these treatments showed that a uniform temperature throughout the solution is necessary. In treatments 5 to 6, water was added as a solvent in the reaction to achieve homogenous temperature. As expected, no tar formation was observed. Among the catalysts tested, nickel catalyst showed the best conversion percentage towards producing alcohols specifically ethanol (table 1). Comparing Treatments 6 and 8, the addition of a reducing gas, hydrogen for this case, did not improve the amount of ethanol in the product.

Determination and Investigation of the Major Process Parameters

The results of the preliminary investigation showed that Raney nickel exhibited the best activity towards producing alcohols among the commercial catalysts tested. Therefore, the next logical step was to investigate the effects of the major process parameters on the production of alcohols with this catalyst. From the previous research project entitled "Thermal Processing of Low-grade Glycerol to Alcohols for Biodiesel Production", results showed that temperature and reaction time were the most influential parameters to the thermochemical conversion of glycerol to products. Similarly, these two parameters are likely to affect the catalytic thermochemical conversion of glycerol to alcohols. The presence of a reducing gas, like carbon monoxide and hydrogen, could play a major role in the catalytic conversion of glycerol to alcohols since reducing gases can strip out oxygen from glycerol. The amount of catalyst was also identified as a major process parameter because the mass of the catalyst correlates to the number of active sites where reactions occur. Lastly, the initial amount of water was also considered since water was determined to be essential in preventing tar formation as discussed earlier. So, experiments were designed to investigate the effects of temperature, the presence of a reducing agent specifically carbon monoxide, reaction time, mass ratio of glycerol and water in the reactant, and mass of the catalyst on the catalytic thermochemical conversion of glycerol to alcohols. To minimize the effect of the type of the catalyst used and the effect of preparation of catalyst, the Raney nickel catalyst used in the experiment came from a single batch.

Three sets of experiments were used in this research project to investigate the effects of the parameters. The first set of experiments examined the effect of reaction time, initial amount of water and mass of catalysts applied in the absence of a reducing gas. The reaction was conducted using a batch reactor. Glycerol, water, and the metal catalyst were mixed into the reactor. Nitrogen gas was used to purge out any oxygen present in the headspace of the reactor. The reactor was then heated to 230°C and maintained at the set reaction time. Afterwards, the reactor was cooled down to room temperature using cooling water. The gases formed during the reaction were removed by opening the exhaust valve. The liquid product collected from the reactor was separated from the catalysts using a vacuum filtration set at constant vacuum pressure of 5 in Hg. Whatman Qualitative No. 2 filter paper was used throughout the experiment.

In the second set of experiments, carbon monoxide was added to determine if the presence of a reducing gas improves the amount of alcohols produced. The experiment was also designed to determine if temperature and initial amount of water affects the reaction. Similar to the previous set, a batch reactor was used and the liquid product was filtered and analyzed using gas chromatogram. The last set of experiments focused on applying the feeder. Batch systems require a preheating period in which reactions can still occur. Fed-batch systems can eliminate preheating of reactants since the reactor can be preheated separately. To configure the existing reactor to a fed-batch reactor, a feeder was installed. The feeder used was an all-purpose pressure vessel reactor from PARR (fig. 1). Its specifications were similar to the reactor, only that it does not have an agitator assembly, pressure transducer, and a cooling system. This feeder can deliver 100 mL of pure glycerol to the reactor for a fraction of a minute by using a pressurized gas as illustrated in Figure 2. This system was used in the previous research project.
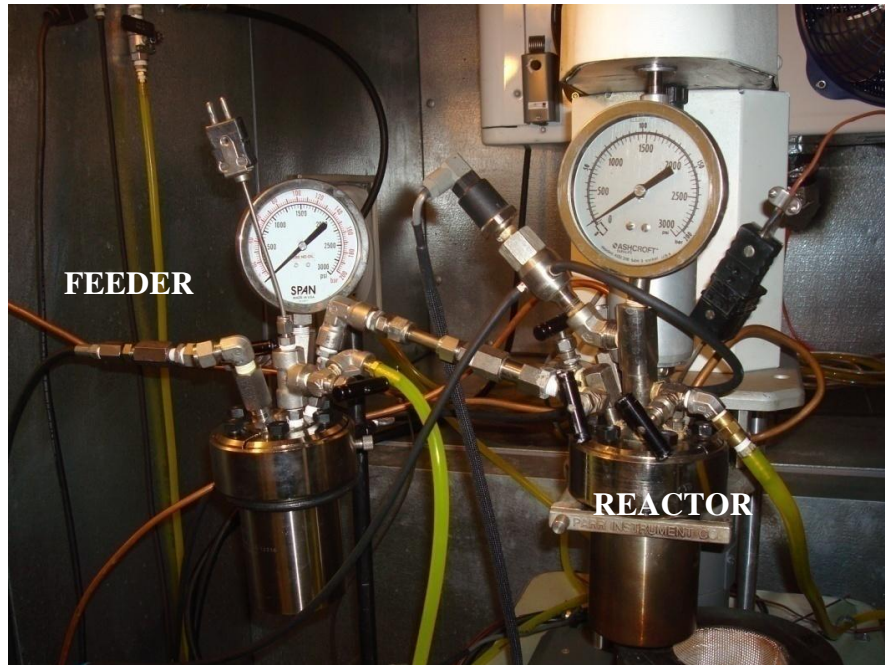
Figure 1: Pressure feeder and reactor setup.
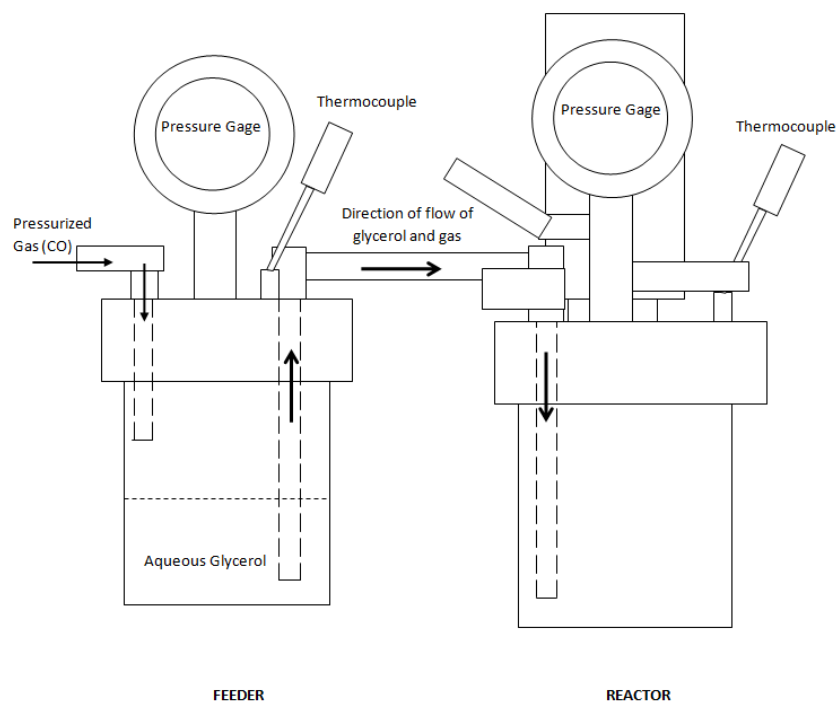
Figure 2: Schematic diagram of the feeder and reactor system.

Effect of Reaction Time

In the absence of a reducing gas, more than 98% of the glycerol was converted to products when the reaction took more than 15 min (table 2). In addition to liquid products, gaseous compounds were also formed during the reaction. The results also show that more gaseous compounds were formed at extended reaction time. Pairwise analysis on the pressure readings using LSD test on SAS suggested that there were significant differences in the amount of gases formed from 15 to 75 min, while no differences were observed from 75 and 105 min of reaction time. This indicates that the total amount of gases formed did not change significantly when the reaction time was extended beyond 75 min.

Table 2: Glycerol Conversion and Gas Formed Using Raney Nickel Catalyst at 230°C

RT (min)	WGMR (mass)	Overall Conversion (%mol)	Gas formed [a] (MPa)
15	1:1	91.1 ± 2.3 %	2.314 ± 0.158
45	1:1	98.6 ± 0.2 %	3.240 ± 0.137
75	1:1	99.6 ± 0.5 %	4.904 ± 0.458
105	1:1	99.9 ± 0.1 %	5.216 ± 0.123
45	7:3	99.9 ± 0.1 %	3.493 ± 0.258
45	3:7	95.3 ± 0.2 %	2.893 ± 0.042

Legends: RT – reaction time   WTGR – Water to Glycerol Mass Ratio
Notes [a]: The difference in the pressure of the reactor measured at 30°C before and after the reaction.

The distribution of the products in terms of percent conversion collected at different reaction times of catalytic thermochemical processing of glycerol using ten grams of Raney nickel (in slurry form) is summarized in Table 3. Up to 6.91% of the initial carbon were converted to ethanol which was an improvement compared to without a catalyst. Other simple alcohols were also produced but only in small amounts. Most of the carbon was converted to gaseous products and a compound identified as propylene glycol.

Table 3: Glycerol Conversion to Alcohols at Different Reaction Time

RT (min)	1-P (%mol)	2-P (%mol)	EtOH (%mol)	MeOH (%mol)
15	0.241 ± 0.018	Not detected	4.074 ± 0.254	0.761 ± 0.086
45	0.388 ± 0.028	0.547 ± 0.425	5.679 ± 0.489	0.886 ± 0.154
75	0.484 ± 0.037	0.161 ± 0.051	5.98 ± 0.912	0.673 ± 0.072
105	0.589 ± 0.018	0.225 ± 0.019	6.91 ± 0.135	0.55 ± 0.023

Legends: RT – reaction time   1-P – n-propanol   2-P – isopropanol
        EtOH – ethanol   MeOH – methanol

Effect of Amount of Water

As discussed earlier, water helps maintain a homogenous temperature profile throughout the solution. Table 4 summarizes the percent molar conversion of glycerol to alcohols at different water to glycerol mass ratios. The amount of ethanol increases as the amount of water in the

solution decreases. A similar trend was observed for methanol. This suggests that increasing the ratio between water and glycerol favors the production of more alcohols. However, the results also showed that increasing the amount of water in the reactant increases the formation of gaseous products. These products consume carbon from glycerol thus decreasing the overall selectivity of the process toward producing alcohols. Although, one advantage of producing gaseous co-products to bio-oil is separating it from the alcohols will be easy.

Table 4: Glycerol Conversion at Different Water to Glycerol Mass Ratios

WGMR (mass)	1-P (%mol)	2-P (%mol)	EtOH (%mol)	MeOH (%mol)
7:3	0.456 ± 0.012	0.149 ± 0.024	7.274 ± 0.258	1.306 ± 0.215
1:1	0.388 ± 0.028	0.547 ± 0.425	5.679 ± 0.489	0.886 ± 0.154
3:7	0.38 ± 0.012	0.065 ± 0.006	4.833 ± 0.217	0.705 ± 0.042

Legends: WGMR – water to glycerol mass ratio
1-P – n-propanol   2-P – isopropanol
EtOH – ethanol   MeOH – methanol

Effect of Amount of Catalyst

Figure 3 shows the trends of selectivity of the process towards the production of alcohols at different amounts of nickel catalysts at 230°C for 45 min of reaction. There was a direct relationship between ethanol selectivity and mass of nickel catalyst used. This observation coincides with the hypothesis that increasing the mass of catalyst increases the total area of the active site where reactions occur. However comparing the results to Table 3, where ten grams of catalyst was employed, there was no significant improvement in the production of alcohols. This suggests that adding more catalyst beyond seven grams does not increase the total area of the active sites. One possible explanation for this is the maximum amount of catalyst that can be suspended in the solution was reached. A customized catalyst or a reconfiguration of the system may solve this limitation. In the case of methanol formation, it was not significantly affected by the amount of catalyst used.
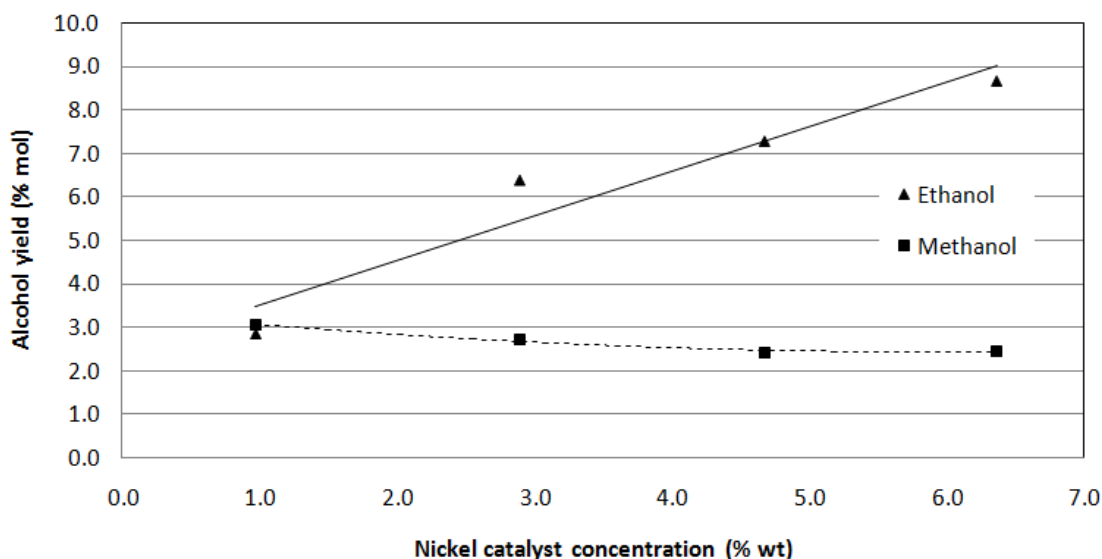
Figure 3: Yields of ethanol and methanol at different Raney nickel catalyst applications.

Effect of Reducing Gas

Table 5 summarizes the molar conversions of glycerol to alcohols using Raney nickel catalyst and carbon monoxide as a reducing agent. In this part of the study, an initial pressure of 200 psi of carbon monoxide was employed. Comparing the results in Table 5 to Table 4, there was no significant difference in the amount of alcohols produced. This suggests that the application of a reducing agent does not affect the reactions that produce alcohols. This also confirms the results obtained from Table 1; there was no difference in the alcohols produced between Treatments 6 and 8. It should be noted that hydrogen was added in Treatment 6 while no hydrogen was supplied in Treatment 8.

Table 5: Alcohol Yields at Different WGMR at 230°C and CO as the Reducing Agent

WGMR (mass)	1-P (%mol)	2-P (%mol)	EtOH (%mol)	MeOH (%mol)
1:1	0.317 ± 0.004	0.119 ± 0.041	5.333 ± 0.254	0.746 ± 0.082
7:3	0.398 ± 0.016	0.154 ± 0.016	7.067 ± 0.293	1.485 ± 0.163

Legends: WGMR – water to glycerol mass ratio
1-P – n-propanol   2-P – isopropanol
EtOH – ethanol   MeOH – methanol

Effect of Temperature

From the previous research project, it was concluded that temperature affects the thermochemical conversion of glycerol. As expected, the results show that the process with the catalyst was affected by temperature (table 6). The only difference was, with the presence of a catalyst, there was a significant increase in the amount of alcohol produced when the temperature was increased. In the previous research project, there was no clear relationship obtained between temperature and amount of alcohols produced only with the conversion of glycerol. Though a portion of glycerol was converted at 200°C, no alcohols were detected in the product while up to 7.65 % of carbon was converted to ethanol at 250°C.

Table 6: Product Yields at 200°C/250°C and CO as a Reducing Agent

T (°C)	1-P (%mol)	2-P (%mol)	EtOH (%mol)	MeOH (%mol)
200	ND	ND	ND	ND
250	0.612 ± 0.02	0.292 ± 0.065	7.65 ± 0.335	0.704 ± 0.085

Legends: T – reaction temperature   ND – not detected
          1-P – n-propanol   2-P – isopropanol
          EtOH – ethanol   MeOH – methanol

Using the feeder and reactor system, same inference was concluded. There was a clear difference in amount of ethanol produced at different reaction temperatures (table 7). Initial reactor temperature refers to the temperature of the reactor with the catalyst right in it before feeding the reactants. After the solution of glycerol and water was fed to the preheated reactor, the temperature was monitored until it stabilized to a certain temperature. This temperature was then set to the temperature of reaction and was controlled by the reactor controller automatically thereafter. It was observed that the temperature change between the initial temperature and the temperature of reaction was also affected by the ratio of water to glycerol in the feed. As expected, higher initial amount of water requires more energy to reach the same reaction temperature.

Table 7: Conversion of Glycerol to Alcohols Using the Feeder System

RUN	Initial T (°C)	T (°C)	WGMR (mass ratio)	RT (min)	MeOH (%mol)	EtOH (%mol)
FED1	250	220	1:1	15	0.368	0.561
FED2	280	220	7:3	15	0.539	0.528
FED3	280	240	1:1	45	0.577	3.580
FED4	250	200	7:3	45	0.671	0.697

Legends: T – reaction temperature   WGMR – water to glycerol mass ratio
EtOH – ethanol   MeOH – methanol

Investigation of Different Supports for Metal Catalysts

In order to explore the effect of different supports in the production of alcohols from glycerol, nickel, and platinum catalyst with different supports were purchased and tested. The criteria used in choosing the type of support to be tested was it must be able to withstand high temperature and pressure. Carbon supported and alumina supported nickel or platinum catalysts have been used in hydrogenolysis and gasification of glycerol to syngas and propylene glycol (Adhikari et al., 2007; Maris and Davis, 2007; Slinn et al., 2008). These processes operate at high temperature and pressure. Thus, alumina and carbon supported metal catalysts are suitable in the thermochemical conversion of glycerol to alcohols.

Platinum (5 %wt) supported on alumina (Pt/Al) and nickel supported on silica-alumina (Ni/Al) were purchased from Alfa Aesar and used in the thermochemical conversion of glycerol to alcohols. Platinum on carbon (Pt/C), which was used in the preliminary tests, was also tested. The reaction was conducted using a batch reactor. Glycerol, water, and the metal catalyst were mixed into the reactor. Nitrogen gas was used to purge out any oxygen present in the headspace of the reactor. The reactor was then heated to 230°C and maintained for 45 min. To investigate the effect of hydrogen in the formation of alcohols, 0.09 g of hydrogen per 100 g of water and glycerol solution was added in the other treatments. In this experiment, a water-to-gas mass ratio of 1:1 and 2 g of catalyst per 100 g of water and glycerol solution were used.

Table 8 summarizes the conversion of glycerol to methanol, ethanol and 1-propanol at different catalyst supports. The amount of ethanol formed in treatments COT1 and COT4 was the highest

among the treatments. This confirms that nickel based catalyst has a higher selectivity towards the formation of ethanol than platinum based catalysts. It is also noticed that the conversion of glycerol to ethanol increased to about 0.4 %mol when hydrogen was added to the system using Ni/Al catalyst. However, the results of the ANOVA (Analysis of Variance) showed that this difference is not statistically significant. The results of the ANOVA also suggest that addition of 0.9 g of hydrogen per 100 g of aqueous glycerol does not have a significant effect on the formation of methanol and 1-propanol. In comparing catalyst activities, the results of the LSD test on SAS suggest that only the comparison between Ni/Al and Pt/Al gave significant difference (results not shown). This means that there is no significant difference in catalyst activity between using a carbon supported and alumina supported catalyst.

Table 8: Alcohol Yields Using Metal Catalysts at 230°C and 45 min

Run	Metal Catalyst	Reducing Gas	Initial Gas Pressure (psig)	Alcohol yields (%mol)		
				Methanol	Ethanol	1-propanol
COT1	Ni/Al	None (N_2)	0	0.452	1.266	0.203
COT2	Pt/Al	None (N_2)	0	0.382	ND	ND
COT3	Pt/C	None (N_2)	0	0.471	0.533	ND
COT4	Ni/Al	Hydrogen	50	0.395	1.665	0.196
COT5	Pt/Al	Hydrogen	50	0.358	ND	0.120
COT6	Pt/C	Hydrogen	50	0.396	ND	ND

Legend: ND- not detected

Investigation of Customized Catalysts

Customized catalysts were also prepared and tested to expand the variability of metal and support combination in finding the best catalysts for producing alcohols from glycerol. In the ease of preparation of the customized catalysts, wet impregnation was chosen to be used in making customized catalysts. This method has been used in studies on glycerol conversion to hydrogen, syngas, and propylene glycol. Nickel catalysts were prepared over two types of supports; (i) cerium oxide (CeO_3) from Nanoscale Materials (Manhattan, KS) and (ii) zeolite. Nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] purchased from Sigma-Aldrich (St. Louis, MO) was impregnated to the supports. A ratio of 10 g of nickel nitrate hexahydrate to 9 g of support

was used in the preparation. The wetted support with nickel solution was then dried at 120°C for 12 h and calcined at 500°C for 6 h (fig. 4). Figure 5 shows the prepared nickel supported on zeolite and nickel supported on CeO_3.

Figure 4: Drying and calcination of customized nickel catalyst using a muffle furnace.

Figure 5: The prepared Ni/zeolite and Ni/CeO_3 catalysts.

In testing the customized catalysts' activity, the pressure feeder and reactor setup was used (fig. 1). Ten grams of the customized catalyst was placed in the reactor while 100 g of water and glycerol solution with 1:1 WTGMR was transferred to the feeder. The catalyst was reduced in the reactor using 50 psig hydrogen and at 200°C for an hour. After the reduction process, the pressure of the reactor was released. The water and glycerol solution in the feeder was then transferred to the reactor using compressed carbon monoxide or hydrogen as illustrated earlier in Figure 2. The two customized catalysts, namely, Ni/CeO_3 and Ni/zeolite, were tested at different reaction temperatures and reducing gases.

Table 9 shows the molar conversion percentages of glycerol to methanol, ethanol and 1-propanol at different treatments. Ethanol was not detected in the product when Ni/zeolite catalyst was used. Using CO as the reducing gas, formation of methanol only occurred in treatments with Ni/CeO_3 catalyst. With these results, it can be concluded that that Ni/CeO_3 is better than Ni/zeolite in converting glycerol to alcohols. The conversion rate of glycerol to products was also better in Ni/CeO_3.

Table 9: Conversion of Glycerol to Alcohols Using Metal Catalysts

Run	Metal Catalyst	Gas/Feeder Pressure (psig)	Reaction Temp. (°C)	Conversion rate (%mol)	Alcohols yields (%mol)		
					Methanol	Ethanol	1-propanol
COM1	Ni/CeO_3	CO/200	240	32.76	0.350	ND	ND
COM2	Ni/Zeolite	CO/200	240	40.78	ND	ND	ND
COM3	Ni/CeO_3	CO/200	300	25.47	0.573	0.565	1.747
COM4	Ni/Zeolite	CO/200	300	34.56	ND	ND	0.081
CCT1	Ni/CeO_3	H_2/100	250	64.44	0.813	0.436	ND
CCT2	Ni/Zeolite	H_2/100	250	21.95	0.870	ND	ND

Legend: ND- not detected

Process Optimization

Based on the results of the investigation on different catalysts and process parameters on the thermochemical conversion of glycerol to alcohols, it can be concluded that temperature, reaction time, and water to glycerol mass ratio influences the ethanol yields of the thermochemical processing of glycerol. Though reaction time affects the ethanol formation (table

3), it is unsafe to operate the reactor at higher than 230°C and reaction time of 75 min and longer. Preliminary runs at 75 min and 250°C using Raney nickel caused the ruptured disc of the reactor to burst due to the build-up of pressure during reaction. Thus for safety reasons, the 45 min reaction time was fixed in finding the optimum conditions in producing alcohols. On the other hand, the comprehensive investigation on different metals supports that customized catalysts lead to the conclusion that Raney nickel was the best catalyst for this application and type of reactor system.

In the optimization of the thermochemical conversion of glycerol to methanol and ethanol, two set of experiments were designed. The first set was to find the optimum water to glycerol mass ratio. In the previous tests, the highest ethanol yield was observed at WTGMR of 7:3 (or 30 %wt of glycerol). The optimum water to glycerol mass ratio might be between 1% and 40%wt of glycerol. Therefore, the levels of the initial amount of glycerol tested were between 10 to 40 %wt of glycerol. The experiment had four levels, namely, 10, 20, 30 and 40 %wt of glycerol. A batch system was used and no reducing gas was added. The second set of experiment was designed to target the optimum temperature. The results in Table 6 show that no alcohols can be produced at 200°C and lower. Thus, the reaction temperature was varied from 210 to 250 °C. It was also hypothesized that the process involves a complex set of reactions and undesired reactions can occur at different temperatures. In order to eliminate these reactions that occur at lower temperatures, the pressure feeder and reactor set up was used. With this set up, the reactor was preheated to the desired temperature which eliminated the heating period. Initially, 100 g of 30 %wt of glycerol solution was added to the feeder. The pressure of the gas, in this case CO, used to push the solution from the feeder to the preheated reactor was set at 200 psig. In both experiments, the reaction time was set at 45 min and 10 g of Raney nickel per 100 g of water and glycerol solution was used.

Figure 6 shows the plot of ethanol and methanol yields at different initial concentrations of glycerol solution. Ethanol yield increases as the initial amount of glycerol increases and leveled off at 30 %wt of glycerol and higher. Ethanol was not detected at 10 %wt of glycerol. Using second-order regression, the optimum water to glycerol ratio was estimated at 1.82 WTGMR (35.47 % of glycerol). At this ratio, an ethanol yield of 11.37 %mol yield can be achieved.
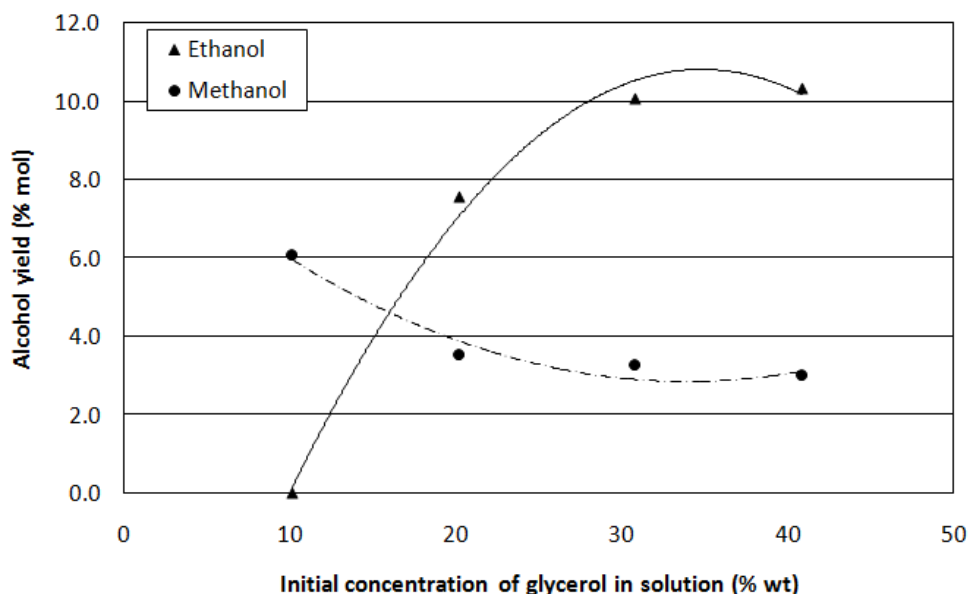
Figure 6: Molar yields of methanol and ethanol vs. initial concentration of glycerol.

On the other hand, the results of the second set of experiments showed that the optimum temperature for the system is 223°C (fig. 7). At this temperature, the ethanol yield was estimated to be 9.51 %mol. Though 4 levels of temperatures were tested, the results of the last level, 250°C, were not included in the analysis since only a fraction of the solution was transferred from the feeder to the reactor. Only 37 g out of 100 g of water and glycerol solution was transferred. The immediate conversion of glycerol to gaseous products during the feeding step caused the reactor pressure to abruptly increase from atmospheric (14.7 psig) to above 200 psig impeding the flow of the solution to the reactor.

For methanol formation, the trend of methanol yield against initial amount of glycerol suggests that the optimum WTGMR is higher than 9:1 (10 %wt of glycerol). In this case, the optimum WTGMR for methanol production was determined. Though further diluting glycerol with water may improve the production of methanol, adding more water to the system will require more energy to heat the reactor making the process inefficient. Using 7:3 WTGMR, the optimum temperature was estimated at 209°C with methanol yield of 4.03 % methanol (fig. 7).
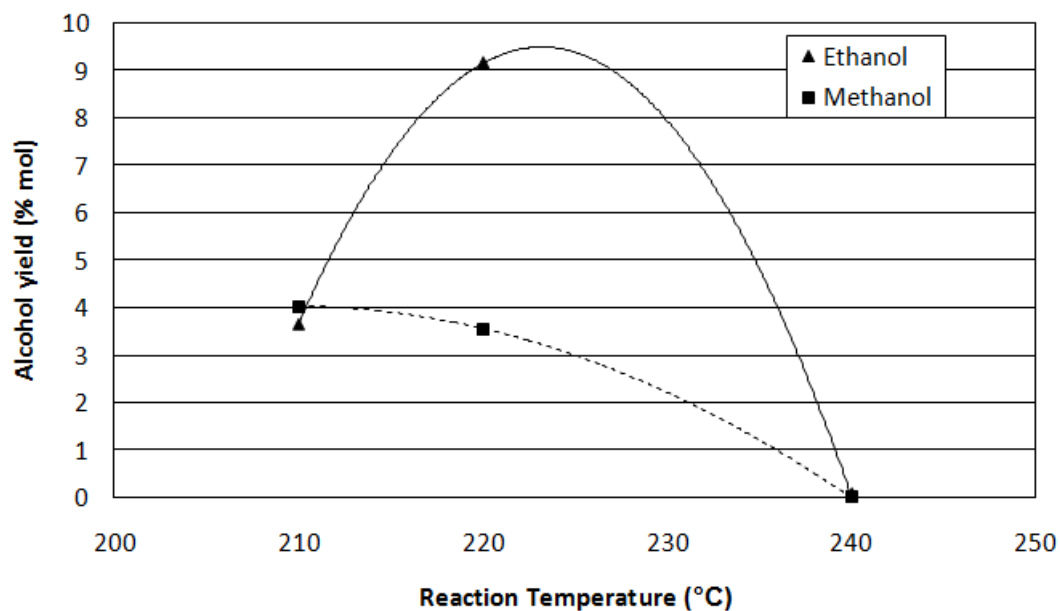
Figure 7: Molar yields of methanol and ethanol at different reaction temperatures.

SUMMARY AND RECOMMENDATIONS

Summary

Commercially available metal catalysts were purchased and tested for their selectivity towards production of alcohols, specifically, methanol, ethanol, and propanol. Among the catalysts tested, Raney nickel catalyst, purchased from Sigma Aldrich, showed the best activity towards producing ethanol. Comparing the results to the data gathered from a previous research project, the addition of metal catalysts greatly improved the selectivity of the process to alcohol formation. Water was also found to be significant in the catalytic thermochemical conversion of glycerol to alcohols. In addition, water also inhibited the production of tar.

Reaction temperature, reaction time, amount of catalyst, and initial water to glycerol ratio were identified to be important in the catalytic thermochemical conversion of glycerol to alcohols. Ethanol production increases at longer reaction time and higher water to glycerol ratios. It was also influenced by mass of catalysts in which a direct linear relationship was observed from one to seven grams of catalysts. However, adding more catalyst will not further improve the productivity of process towards alcohols, since there is a limitation on how much catalyst can be suspended in the solution. On the other hand, methanol formation was only significantly affected by the initial amount of water in the reactant. In the case of reaction temperature, the results in both batch and fed-batch experiments suggested that reaction temperature influences the production of alcohols, specifically ethanol. The optimum conditions in producing ethanol was found out to be at 1.82 WTGMR and 223°C for 45 min of reaction and using 10 g of Raney nickel catalyst per 100 g of solution. The highest estimated yield of ethanol at optimum was 11.37 %mol.

Recommendations for Future Research

The results of the research project showed that ethanol can be selectively produced from glycerol via thermochemical conversion process using metal catalysts without the formation of tar and char. Though the reactor system used in this research project only achieved an ethanol yield of up to 11.37 %mol, other reactor system, such as continuous reactors and reactive distillation, may improve this yield. Continuous reactor systems can employ recycling to increase the production of ethanol and methanol. Reactive distillation can simultaneously remove the desired

products, e.g. methanol and ethanol which will shift the reaction towards producing more alcohols. Therefore, a study on reactive distillation and/or continuous reactor systems are recommended for future research.

APPENDIX

Student Involvement

A graduate student and two undergraduate students participated in conducting this research project. Randy Maglinao, a graduate student of Biological and Agricultural Engineering at University of Idaho, was responsible for managing, designing and conducting experiments, and data collection and analysis. He also directly supervised two undergraduate students, Sonam Sherpa and Sushant Kshetri, who assisted him in data collection and experimental operations.

As a graduate student, the research project gave Randy Maglinao the opportunity to integrate his education in chemistry, engineering, and biology to scientific research in bioenergy and biorefinery. The project also provided assistance in his pursuance of a doctoral degree in Biological and Agricultural Engineering. The experiences acquired from this research project are preparing him for his professional career growth as scientist and engineer in this field. Supervising undergraduate students in conducting the experiments helped him to acquire management skills that will be beneficial for his future occupation as a research scientist, a faculty, or a project leader in the field of biological and agricultural engineering. It also gave him the opportunity to learn the skills to plan and execute experiments and other tasks for the purpose of completing a project and achieving its goals in a specified time period. This project provided him the experience of holding lectures in class and writing technical papers and presenting it through oral and poster presentations in professional technical conferences. With this project, he was able to present two papers entitled "Thermochemical Conversion of Glycerol from Biodiesel Production to Primary Alcohols" and "Recent Developments in Chemical Processing of Glycerol to Value-Added Products" to the Annual International ASABE meeting held this year in Pittsburg, PA.

Sonam Sherpa and Sushant Kshetri, both majoring in Material Science at University of Idaho, learned the proper techniques and methods in handling chemicals and conducting experiments in a laboratory. They became skilled in using common laboratory equipment for both qualitative and quantitative analysis that would be beneficial in their studies and senior design/research projects. This research project also provided them the knowledge of the applications of the

theories that they learned in their classes like chemical reactions, thermodynamics, and chemical structures to real world problems in bioenergy and biorefinery.