THERMAL PROCESSING OF LOW-GRADE GLYCEROL TO ALCOHOLS FOR BIODIESEL FUEL PRODUCTION, PHASE II

Final Report

KLK 754

N10-01

National Institute for Advanced Transportation Technology

University of Idaho

Dr. B. Brian He

January 2010

DISCLAIMER

1. Report No.	2. Government Accession No.	3. Recipient’s Catalog No.

4. Title and Subtitle Thermal Processing of Low-Grade Glycerol to Alcohols for Biodiesel Fuel Production, Phase II	5. Report Date January 2010
	6. Performing Organization Code KLK754
7. Author(s) He, Dr. B. Brian	8. Performing Organization Report No. N10-01
9. Performing Organization Name and Address National Institute for Advanced Transportation Technology University of Idaho PO Box 440901; 115 Engineering Physics Building Moscow, ID 838440901	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: August 2008– January 2010
	14. Sponsoring Agency Code *USDOT/RSPA/DIR-1*

Supplementary Notes:

16. Abstract

Conversion of crude glycerol to value added products can broaden its use and ultimately reduce the cost of biodiesel production. During the second year of the project, results from previous experiments were used to comprehensively investigate the thermochemical conversion of glycerol. A surface response experiment was conducted to find out the optimum temperature and reaction time. Statistical results showed that the highest ratio of bio-oil to char could be produced at temperature and reaction time of 320°C and 195 minutes. However, the amount of alcohols produced varied significantly such that no clear correlation between these two parameters with respect to the production of alcohols can be concluded. This variation of data suggests that the process involves a complex set of reactions. Nevertheless, a simple first-order kinetics model was able to describe the conversion of glycerol to the different products. A thorough investigation on the effect of initial pressure and type of reducing agent with an improved feeding system were conducted. Results showed that thermochemical conversion of glycerol occurs at 300°C or higher for 60 min, and that the initial pressure and type of reducing agent does not have a significant effect. The results gathered in the project gave sufficient evidence that the thermochemical of glycerol could produce methanol, ethanol and propanol. However, further studies should be conducted to improve the efficiency of the process. An investigation on applications of metal catalysts and reactive distillation technique is under conduction to further explore the parameters affecting process efficiency and the process optimization.

17. Key Words Biodiesel fuels, alternate fuels, fuel processing	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 34	22. Price ...

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

TABLE OF CONTENTS

FIGURES

EXECUTIVE SUMMARY

The conversion of crude glycerol to other value added products can broaden its use and ultimately reduce the cost of biodiesel production. Crude glycerol is the major by product of biodiesel production, and its conversion to methanol, ethanol and propanol could enhance its value. Methanol can be used back in the production of biodiesel from transesterification of vegetable oils. Ethanol can also be utilized as an alternative reactant to methanol in the production of biodiesel. In thermal conversion, three general processes have been utilized, but liquefaction was preferred because it favors the conversion of organic compounds to liquid products in which the desired alcohols may be found. This report provides the highlights of the activities conducted and the results gathered from the project entitled “Thermal Processing of Low-grade Glycerol to Alcohols for Biodiesel Production”.

During the first year of the project, a reactor system was designed and constructed. The system has a 300 mL PARR 4560 Mini Bench Top Reactor, which was purchased from PARR Instruments. A metal-framed chamber with carbon monoxide alarms was also constructed as part of the reactor system. Preliminary tests helped to refine the procedures in operating the reactor system.

Analytical methods were developed for Agilent 6890N Series Gas Chromatograph with Flame Ionization Detector (FID) and High-Performance Liquid Chromatograph (HPLC). Both equipments are available in the Biological and Agricultural Engineering laboratory. The development of these methods was necessary in order to determine the amount glycerol left and alcohols produced during the reaction. The procedures were refined and corrected based on the information gathered from preliminary tests. The methodology developed for HPLC successfully determined the amount of glycerol in a sample but not methanol, ethanol and propanol. On the other hand, the gas chromatograph (GC) was able to simultaneously detect methanol, ethanol, 1-propanol, 2-propanol and glycerol in the samples. Relative standard deviation (RSD) values suggest that the results using the gas chromatograph deviated less than using the HPLC. Thus, the procedures developed in the gas chromatograph were used in the research.

The major process parameters were identified through literature research and evaluated by conducting preliminary experiments. Reaction temperature, initial pressure of the reducing agent, time of reaction and type of reducing agent were identified as the major parameters. The parameters were screened over a wide range of reaction conditions through batch and fed-batch experiments. Results showed that temperature and time of reaction significantly affect the thermochemical conversion of glycerol to alcohols.

During the second year of the project, the results from the first year were used to comprehensively investigate the thermochemical conversion of glycerol to alcohols. A surface response experiment was designed and conducted to find out the optimum temperature and reaction time for the thermochemical conversion of glycerol to products. Statistical results showed that the highest ratio of bio-oil to char could be produced at temperature and reaction time of 320^{o}C and 195 minutes, respectively. However, the amount of alcohols produced varied significantly such that no clear relationship between these two parameters with respect to the production of alcohols can be concluded. This variation of data suggests that the process involves a complex set of reactions. Nevertheless, a simple first-order kinetics model was able to describe the conversion of glycerol to the different products.

A thorough investigation on the effect of initial pressure and type of reducing agent and fed-batch experiments with a better feeding system were also conducted. The results gave strong evidence that initial pressure and type of reducing agent do not have significant effect on the amount of bio-oil and alcohols produced. Moreover, data gathered confirmed that thermochemical conversion of glycerol occurs at over 300^{o}C with reaction time longer than an hour.

The results gathered in the project gave sufficient evidence that the thermochemical process could produce methanol, ethanol and propanol from glycerol. However, further studies should be done to improve the efficiency of the process. An investigation on the effect of metal catalysts or using reactive distillation systems is recommended for further research.

BACKGROUND

The economic competitiveness of biodiesel against fossil fuels is very much affected by the disposal and utilization of its major by product, crude-glycerol. With the increasing production of biodiesel, an increasing supply of glycerol is expected, which will then consequently decrease its value. Thus, the conversion of glycerol to other value added products can broaden its use, increase its demand and ultimately reduce the cost of biodiesel production.

Thermochemical conversion of glycerol to primary alcohols is a potential process to increase the value of crude glycerol. Thermochemical conversion uses heat and applies chemical reagents to breakdown crude glycerol into simpler compounds. Primary alcohols are organic compounds that have a hydroxyl group at one end of the carbon chain. Glycerol 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 structure will produce primary alcohols. Methanol, the simplest primary alcohol produced from glycerol, can be used as a reactant in the production of biodiesel from triglycerides. Other alcohols, such as ethanol, propanol, and *iso*-propanol, can also be used as an alternative reactant to methanol in the production of biodiesel. Thus, finding ways of producing primary alcohols from glycerol is of significance.

There are three general thermochemical processes, namely, gasification, pyrolysis and liquefaction[1]. Among these processes, pyrolysis and liquefaction produce relatively high percentage of hydrogenated oils, in which methanol and ethanol may be found. Both processes use heat and oxygen-absent conditions. Pyrolysis operates at atmospheric pressure and relatively higher temperatures (400 to 600°C) while liquefaction operates on relatively moderated temperatures (300 to 400°C) and higher pressures (720-2900 psi). Moreover, liquefaction favors the conversion of organic compounds to liquid products and minimizes the production of char compared to pyrolysis. With this, liquefaction is preferred in producing liquid products.

A feasibility study supported by a NIATT UTC grant has shown that methanol, ethanol, 1-propanol and 2-propanol could be obtained through liquefaction process. However, detailed in-

---

[1] A.V. Bridgwater. 1999. Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of Analytical and Applied Pyrolysis*. 51: 3–22.

depth investigation had not been conducted. Influential parameters had not been identified and their effects had not been explored. In addition, the favorable conditions for the thermochemical conversion to proceed had not been determined. Thus, an applied research entitled “Thermal Processing of Low-grade Glycerol to Alcohols for Biodiesel Production” was proposed and approved and supported by NIATT to address these questions.

OBJECTIVES

This research project aimed to conduct a process investigation on glycerol thermochemical conversion, and an engineering evaluation of the technology. The results obtained from this project will be added to the current knowledge base on the utilization of crude glycerol and may be used by the whole biodiesel industry. Specifically, the objectives of the project are the following:

1. To develop and test a reactor system that is capable of conducting high temperature, high pressure chemical reaction of thermochemical conversions,
2. To build a chamber that will harness the pressure reactor,
3. To develop analytical procedures for detecting and identifying the products from the thermochemical conversion of glycerol,
4. To identify major parameters that affect the thermochemical conversion of glycerol to alcohols,
5. To conduct a thorough investigation on the effects of the identified parameters on the thermochemical conversion,
6. To determine the optimum conditions based on statistical models to achieve the best glycerol conversion and alcohol yield, and
7. To compare the experimental data gathered with kinetic reaction equations.

REACTOR SYSTEM

The reactor system was necessary for the project. In the development of the reactor system, the design considered the extreme conditions of the reaction such as high temperature, high pressure and possible production of organic chemical acids. In addition, the reactor system should have precise temperature and pressure controls, adequate agitation with control, a liquid and gaseous sampling mechanism, and safety features for unanticipated reactor failure.

Development of the Reactor System

A 300 mL PARR 4560 Mini Bench Top Reactor was purchased and used for this research (see Figure 1). This reactor can handle up to 3000 psi of pressure and 350°C for temperature. It is controlled by the 4857 Reactor Controller that has PC-based software for the control of temperature and motor speed (or agitation speed). The controller measures temperature, pressure and motor speed using a dual thermocouple, pressure transducer and tachometer, respectively. For safety measures, a metal-framed chamber was constructed to isolate the reactor if gas leakage or an unexpected explosion occurs during the experiment. A schematic drawing illustrating the gas and cooling water piping and cables for the control is shown in Figure 2. All the main valves, switches and the control console, PARR 4857 Reactor Controller, were placed outside the chamber for easy access.

Figure 1: PARR 4560 mini bench top reactor.

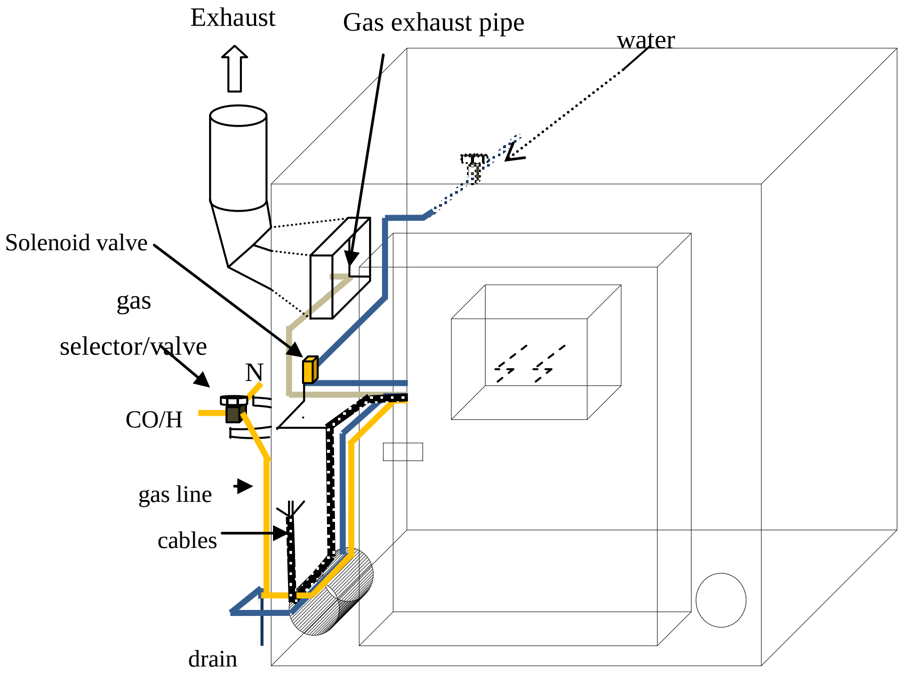

Figure 2: Schematic diagram of the reactor's chamber.

Figure 3 shows the metal-framed chamber with the connections and gas tanks. The copper pipes deliver cooling water to the reactor and direct excess gases to the exhaust. In addition, two carbon monoxide alarms were installed to notify researchers if a CO leakage occurs and if the carbon monoxide levels in the surroundings become toxic. One alarm was placed inside the chamber and the other was installed outside. Operating procedures were formulated according to the manufacturer's manual. The operating procedures were then refined through preliminary tests using water and glycerol. These tests were conducted to also identify any problems such as gas leaks.

Preliminary Test Results on the Reactor System

Preliminary tests using water were conducted to identify any problems such as gas leaks. The tests showed no immediate problems for using the reactor system for the research. The preliminary tests also provided information to refine the procedures in operating the reactor system.

Figure 3: The constructed metal-framed chamber.

Preliminary tests using glycerol were performed using the developed procedures. Results showed that the average heating rates were roughly 10°C/minute which is the usual rate in liquefaction (National Science Foundation, 2008). It also showed that the reactor system can sustain the reactor's temperature within the 2°C range.

ANALYTICAL PROCEDURES IN DETERMINING GLYCEROL AND ALCOHOLS

Appropriate analytical methods are necessary to be able to determine the amount of glycerol left and alcohols produced during the reaction. While there are established standards and analytical procedures in the determination of alcohols and glycerol, there are no standard procedures yet specific for determining methanol, ethanol, propanols and glycerol in their mixtures. Gas chromatography is typically used with high resolving power and unquestionable reproducibility and repeatability in determining alcohols in fuels. It has also been used in determining small amounts of glycerol in biodiesels (ASTM, 2007). Thus, gas chromatography could very well be a potential analytical method in measuring the concentrations of the various components of the product mixture necessary in studying the thermochemical conversion of glycerol to alcohols.

Development and Evaluating Analytical Procedures

The Department of Biological and Agricultural Engineering's laboratory has both gas chromatography (GC) and High-Performance Liquid Chromatography (HPLC). Thus, both were utilized for detecting glycerol, methanol, ethanol, 1-propanol and 2-propanol individually and in their mixtures. The information gathered from secondary research provided the starting point in the development of the methodologies for gas chromatography and HPLC. Alltech Altima C18 and Ultracarb columns were used in the high-performance liquid chromatography while DB-wax column was purchased and used in the gas chromatography. Preliminary runs were performed to refine the methodology.

Comparison between High Performance Liquid Chromatography and Gas Chromatography

The methodology developed for HPLC successfully determined the amount of glycerol present in the sample but not methanol, ethanol and propanol. These compounds were not detected because Evaporative Light scattering Detector (ELSD), which is the detector used by the HPLC, cannot detect volatile compounds. On the other hand, GC uses Flame Ionization Detector (FID) which was able to detect all the compounds present in the sample. Table 1 summarizes the computed relative standard deviations (RSD) of each compound and determination methods. The RSD values suggest that the results using the GC deviated less than the results using the HPLC. Moreover, the deviations on the responses in determining glycerol, ethanol and methanol did not differ much.

Another problem in using the HPLC in determining glycerol and other alcohols is that the response differed from day to day as shown in Tables 2 and 3. The p-value for the HPLC was less than 0.05. This suggests that results in the HPLC significantly varied between days while the results in the GC did not. One possible explanation for the variation in the HPLC is that the HPLC used in this experiment is old and some parts may not be functioning properly.

Table 1: Relative standard deviations of the compounds through different determination methodologies

Compound of interest	Relative Standard Deviations (%)	
	HPLC with Alltech Altima C18 column	**Gas chromatogram with DB-wax column**
Glycerol	4.712	3.284
Methanol	---NA---	3.836
Ethanol	---NA---	3.216

Table 2: ANOVA results on the day-to-day comparison using HPLC

Source	DF	Type III SS	Mean Square	F Value	p-value
Day	2	3.085	1.542	17.79	**0.0007**
Amount	5	62.18	12.44	143.4	**<.0001**

Table 3: ANOVA results on the day-to-day results using gas chromatography

Source	DF	Type III SS	Mean Square	F Value	p-value
Day	1	1.270E11	1.270E11	0.44	**0.5434**
Amount	4	1.433E14	3.582E13	124.0	**0.0002**

Refining the Analytical Procedure

Figure 4 shows the plot of the computed response area on the gas chromatogram against the amount of glycerol. The trend of the plot shows that it curves at more than 600 mg of glycerol. This means that the methodology developed in the gas chromatography can only accurately determine the amount of glycerol up to 600 mg. The reason for this limitation is the lower solubility of glycerol to diethyl ether-pyridine solution. This inference was confirmed when approximately five grams of glycerol was prepared. Two layers of liquid were observed and the bottom layer is presumed to be undissolved glycerol . This limitation was not observed for ethanol, methanol and propanol. The relatively low solubility of glycerol to the solvent resulted in a lower sensitivity in detecting alcohols since only small amounts of the sample can be prepared. Therefore, it was necessary to find an alternative solvent.

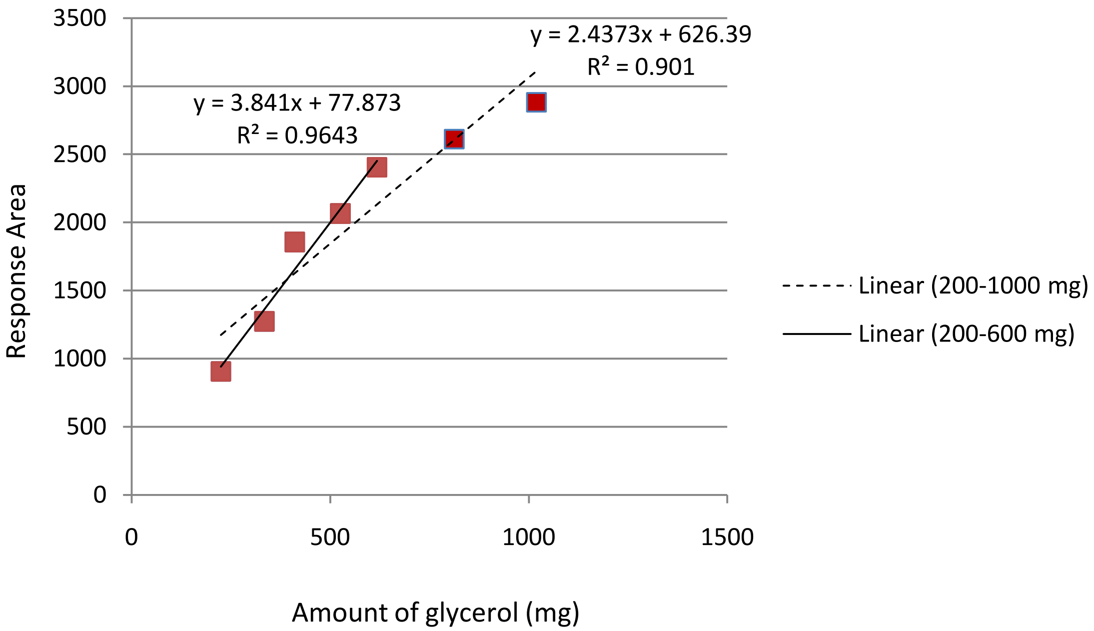

Figure 4: Plot of response area on the gas chromatogram against amount of glycerol using ethyl ether-pyridine solvent.

Through literature research, acetone-water solution was found to have better dissolving power towards glycerol and other organic compounds that are typically found in pyrolysis oil. The solubility of glycerol was tested by preparing approximately five grams and using the same preparation procedures but acetone and water as solvents. The result of the test showed a complete dissolution of glycerol. The plot of the computed response area against the amount of glycerol prepared also exhibited a linear plot during GC calibration as shown in Figure 5. This verifies that using the alternative solvent solution can be used in detecting a wider range of amount of glycerol.

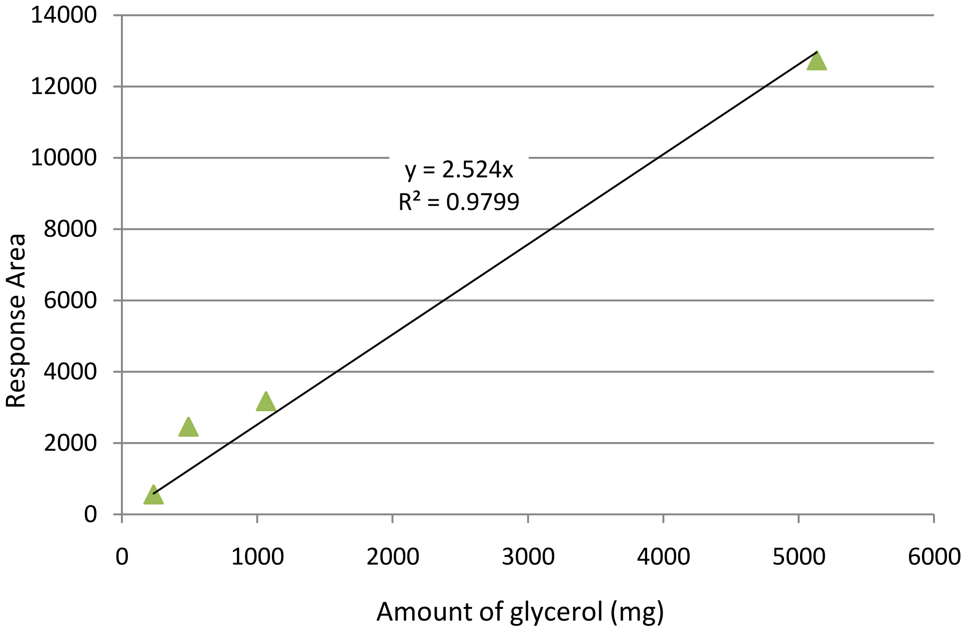

Figure 5: Plot of response area on the gas chromatogram against amount of glycerol using acetone-water solvent.

PRELIMINARY INVESTIGATION ON PROCESS PARAMETERS

The major process parameters were initially identified through literature research and preliminarily evaluated by conducting test runs.

Identifying Major Process Parameters

Reaction time and temperature, initial pressure of the reducing agent, and the type of reducing agent were initially identified as major process parameters for the thermochemical conversion of glycerol to alcohols. In thermochemical conversion, heat is provided to break down the chemical bonds of a compound and produce free radicals that will eventually attack compounds to form simpler ones. Temperature of the reaction plays an important role in converting chemicals like glycerol into simpler compounds. As the temperature increases, more energy is provided or made available for the reaction. Studies reported that at atmospheric pressure, glycerol undergoes thermochemical conversions at temperatures higher than 430°C (Hurd, 1929). But there are no studies yet on the effect of temperature at elevated pressure and with a reducing agent.

As the pressure indicates how much mass of the reducing compound is present on a specified volume, the initial pressure of the reducing agent could very well play a major role in the thermal conversion of glycerol. Higher initial pressure means more reducing agent is available for the reaction. In addition to the pressure, the type of reducing agent used and the time of reaction are other important factors in the process. However, their effects on the thermochemical conversion of glycerol have yet to be explored.

Evaluating the Identified Process Parameters

As one of the objectives of the research, preliminary experiments were conducted to explore the wide range of reaction conditions to evaluate the major process parameters. So, experiments were designed to investigate the effects of temperature, initial pressure of the reducing agent, reaction time and type of reducing agent on the thermochemical conversion of glycerol. The first experiment was intended to determine whether thermochemical conversion of glycerol occurs faster similar to what happens during fast pyrolysis. The three parameters were studied with a 2^3 factorial experimental design as summarized in Table 4. The levels of temperature used in the experiment were 280°C and 330°C which are the claimed thermal decomposition temperature of glycerol and the near the maximum temperature limit that the reactor can operate, respectively.

The initial pressure of the carbon monoxide (CO) which reflects the initial number of moles of the reducing agent was set at 50 and 200 psi.

Table 4: Factorial experimental design matrix in studying the thermo-chemical conversion of glycerol

Treatment	Temperature (°C)	CO/ initial pressure (psi)	Reaction time (min)
1	330	200	5
2	330	200	1
3	330	50	5
4	330	50	1
5	280	200	5
6	280	200	1
7	280	50	5
8	280	50	1

A fed-batch reactor system was also designed and used to determine whether repolymerization occurred during the first experiment. Repolymerization is a process where a compound breaks down into fragments at lower temperature and forms polymerized compounds (Whitehurst, 1938). These polymerized compounds do not decompose at higher temperatures which prevents the production of the desired liquid fuel products. The fed-batch reactor system has an inlet system that was connected to the reactor’s sampling port. The inlet system was composed of Eldrex pump which can deliver 30 mL/minute of water and can operate up to 3000 psig. However, due to the high viscosity of glycerol at ambient temperature, glycerol was preheated to 70°C in order to increase its flow rate into the reactor. The schematic drawing of the reactor’s preheater-mass scale set up is illustrated in Figure 6. The procedure used in the fed-batch experiment was similar to the first experiment.

The third set of runs used a fractional factorial experimental design as shown in Table 5. This design was chosen because it is appropriate for conducting preliminary screening of parameters. This set used similar temperature settings as the first set while initial pressures of carbon monoxide were set at 200 and 340 psi. Moreover, time of reaction was prolonged to 3 hours and 6 hours. This set of runs was designed in order to determine whether thermochemical conversion of glycerol occurs slowly at longer reaction time.

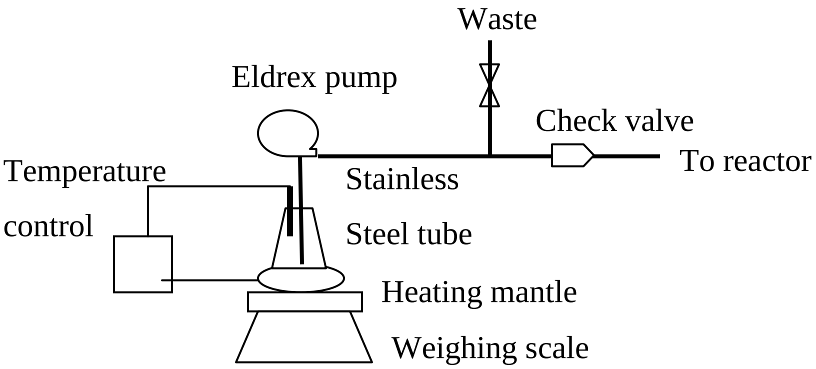

Figure 6: Schematic drawing of the inlet system of the fed-batch reactor.

Table 5: Fractional factorial experimental design matrix in studying the thermo-chemical conversion of glycerol at longer time of reaction

Treatment	Temperature (^{0}C)	CO/ initial pressure (psi)	Reaction time (mins)
9	280	200	180 (3 hours)
10	330	340	180 (3 hours)
11	330	200	360 (6 hours)
12	280	340	360 (6 hours)

Effects of reaction time and temperature

The thermochemical conversion of glycerol did not occur within 5 minutes of reaction at both 280 and 330°C temperature and 50 and 200 initial pressure of carbon monoxide as the reducing agent. In 5 minutes of reaction time, glycerol remained colorless and viscous in all the treatments (1-8) as shown in Figure 7. Moreover, bio-oil and char were not produced. On the contrary, all liquid samples collected after reaction times of 3 and 6 hours (treatments 9-12) were yellowish to brownish in color (Figure 8). The color of the samples can be attributed to the presence of other chemicals formed during the reaction. Char and bio-oil were both produced in treatments 10 and 11. On the average, 47% by weight was bio-oil and had a viscosity similar to water. As expected, the char produced solidified in just a few days.

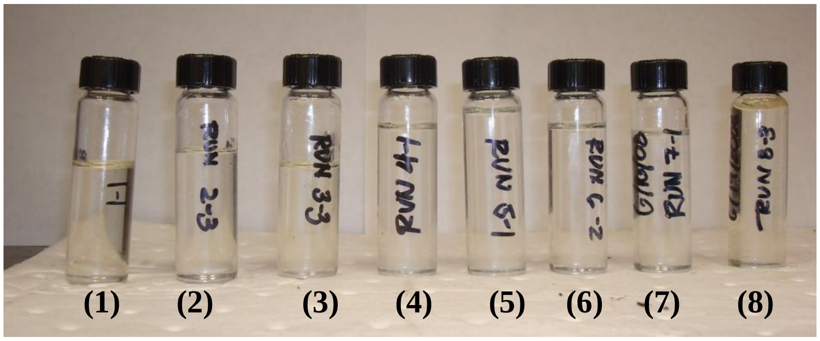

Figure 7: Glycerol after one minute and 5 minutes of reaction at different treatments.

Effects of initial pressure of the reducing agent

Statistical analysis did not give enough evidence that the effect of the initial pressure of carbon monoxide as the reducing agent is significant. This may suggest that carbon monoxide is in excess for treatments 9 to 12. This estimated error was used to estimate the t-statistic values of each treatment (Table 6).

Table 6: Results of t-tests using Lenth's pseudo-standard error

Source	T-statistic	$T_{critical}$ ($t_{0.05,1}$)	Result of the test
BC = A	6.980955	6.314	Reject
AC = B	0.837281	6.314	Failed to reject
AB = C	0.496052	6.314	Failed to reject

Legend: A = Effect of temperature effect; B= effect of CO Pressure; C = effect of time

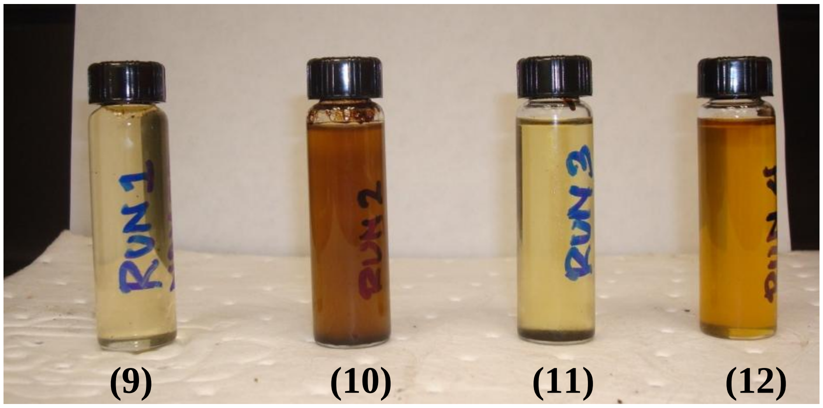

Figure 8: Glycerol after 3 hours and 6 hours of reaction at different treatments.

Figure 9 shows the fresh char formed during the reaction. The samples collected from treatments 9 and 12 did not have char and bio-oil but only a single phase viscous liquid. The viscosity of the samples indicates that most of the glycerol did not undergo thermochemical conversion to simpler compounds. It should be noted that treatments 10 and 11 had a higher reaction temperature of 330°C as compared to 280°C in treatments 9 and 12. The formation of char and bio-oil in the second set of runs but not in the first set gives enough evidence that time of reaction affects the thermochemical conversion of glycerol.

Fed-batch reactor system

The results in the fed-batch experiment were similar to the first batch of the experiment. The reaction did not produce bio-oil and char as expected. However during the analysis of the reacted glycerol using gas chromatography, unidentified peaks were observed. Peaks at residence times of 11-12 minutes were noticed in the chromatogram. These unidentified peaks can have a boiling point higher than the alcohols and pyridine which is 115.2°C. The compounds that caused these peaks could be a semi-volatile organic compound formed when some of the glycerol were heated instantaneously as glycerol flows to the hot vessel. Further research is still needed to identify these unknown peaks. It was also noticed during the experiment that the flow of glycerol in the inlet system was slow. Viscosity and high pressure of the reactor may have influenced the pumping system.

Figure 9: Char produced during thermochemical conversion of glycerol to products.

Effect of the type of reducing agent

When hydrogen was used as the reducing agent in the thermochemical conversion of glycerol, similar results were observed. The sample collected also contained char and bio-oil. The bio-oil was approximately 45.79% by weight. The color of the bio-oil was much darker compared to the bio-oil collected from treatments 10 and 11 as shown in Figure 10. It is not yet known what causes the discrepancies in color. Based on these results, carbon monoxide or hydrogen as the reducing agent did not significantly affect the thermochemical conversion of glycerol. However, further studies are still needed to have substantial evidence for this inference.

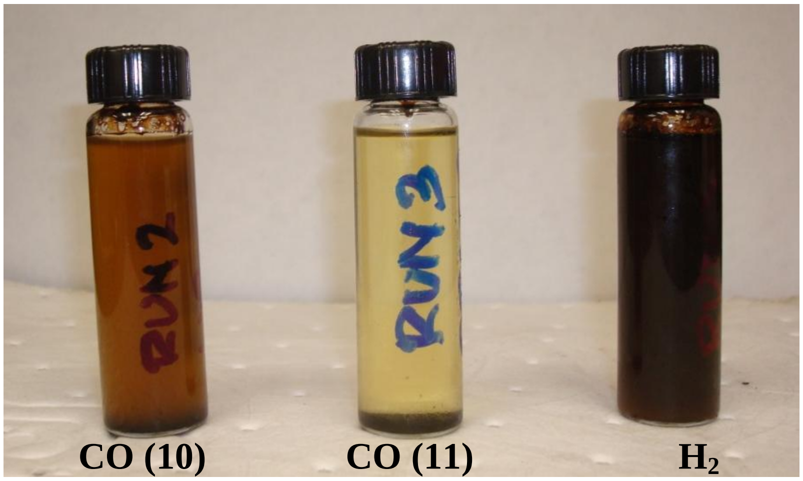

Figure 10: Bio-oil collected from the thermo-chemical conversion of glycerol using different reducing agents.

Effects of the Operating Parameters on the Production of Alcohols

The GC results using diethyl-ether and pyridine as the solvent showed that methanol, ethanol, and propanol were not detected. However, when the mass of samples that were prepared and diluted using the acetone and water solvent system were increased ten times, small amounts of methanol, ethanol and 1-propanol were detected in some of the treatments although 2-propanol was still not detected. Table 7 shows that treatments 10 and 11 produced relatively higher amounts of methanol, ethanol and 1-propanol. Lenth’s pseudo-standard error analysis showed that only 1-propanol rejected the null hypothesis (see Table 8). This gave enough evidence that the temperature significantly affected the production of 1-propanol. On the other hand, the results did not give enough evidence that the effect of the initial pressure of carbon monoxide and time of reaction are significant for the production of alcohols. In addition, the results also suggest that there were no significant effects of temperature on the production of methanol and ethanol. It is possible that their formation might have been affected by combined effects rather than by a single operating parameter.

Table 7: Mass percentages of alcohol produced

Treatment	Alcohol produced (%wt)		
	Methanol	Ethanol	1-Propanol
9	0.16	ND	0.015
10	0.22	0.38	0.42
11	0.27	0.71	0.49
12	0.11	ND	0.075

ND = not detectable.

Table 8: Results of t-tests using Lenth's pseudo-standard error for different alcohols

Compound	SOURCE		
	BC=A	AC=B	AB=C
Methanol	3.018 (FR)	1.317 (FR)	0.0159 (FR)
Ethanol	2.167 (FR)	0.6667 (FR)	0.6667 (FR)
1-Propanol	7.327 (R)	1.198 (FR)	0.1350 (FR)

Legend: A = effect of temperature; B= effect of CO Pressure; C = effect of time; R- Reject null hypothesis; FR = Failed to reject the null hypothesis

Note: The results of statistical analysis were compared to critical value of 6.314 which was obtained from the Studentized t-table at 90% confidence level, two-tail test and degrees of freedom of 1.

THOROUGH INVESTIGATION AND OPTIMIZATION OF THE PROCESS PARAMETERS

The results of the preliminary investigation provided information that temperature and time of reaction affect the thermochemical conversion of glycerol significantly. However, further studies were needed to sufficiently evaluate the effects of initial pressure and the best type of reducing agents for the reaction. Thus in the second year, the project continued with determining the optimum temperature and reaction time for conversion of glycerol to alcohols and thorough investigations on the effects of the remaining two parameters. Moreover, a better feeding system was designed, built and tested to explore the effect of temperature lag on the conversion of glycerol to alcohols.

Optimization of Reaction Temperature and Reaction Time

In order to determine the optimum temperature and reaction time for maximum production of alcohols and conversion of glycerol, a response surface experiment analysis, specifically, central composite design was used. This design assumes that the input factors and responses have a second-order relationship. The values of the parameters in the experimental matrix were formulated using the data gathered from the preliminary investigation and the limitation of the reactor system as shown in Table 9. In this experiment, bio-oil and alcohol production and conversion of glycerol were selected as the response variables. Char and bio-oil were separated using cold vacuum filtration in order to determine the mass of bio-oil produced. Mass percentages of methanol, ethanol and propanol produced, and residual glycerol were determined using gas chromatograph. The results were then encoded and analyzed using SAS program.

Optimum Conditions for Thermochemical Conversion of Glycerol to Alcohols

Table 10 summarizes the results of the ANOVA for the master model and predictive model for the thermochemical conversion of glycerol to bio-oil. The master model represents the complete quadratic model which includes the effects of the temperature and time and its combined effects. However, not all the parameters are significant in predicting the response. In this case, the computed p-value for the combined effect of temperature and time strongly suggests that it is insignificant (p-value of 0.89358). This conclusion was based on a 90% confidence level. In statistics, a p-value that is lower than 0.1 means that there is sufficient evidence that a parameter is significant in the model. Because the time parameter has a p-value very close to 0.1 and its second-degree effect is significant, it was included in the predictive model. The final predictive model included four parameters.

Table 9: Response surface experimental design matrix in optimizing the thermo-chemical conversion of glycerol

Treatment	Temperature (°C)	Reaction time (min)
C1	310	95
C2	340	120
C3	268	180
C4	310	180
C5	310	180
C6	310	180
C7	340	240
C8	352	180
C9	310	265
C10	310	180
C11	280	120
C12	280	240
C13	310	180

Table 10: Results of the ANOVA and effect estimates of the master model and predictive model for the production of bio-oil

Source	Master Model		Predictive Model	
	Effect Estimate	p-value	Effect Estimate	p-value
Temperature (T)	16.51	0.02249	16.51	0.01436
Time (t)	9.524	0.1363	9.524	0.1101
T^2	-26.44	0.003327	-26.44	0.001642
T•t	-1.107	0.8938	---	---
t^2	-18.31	0.01947	-18.31	0.01222

Note: T^2 and t^2 represents second-degree variables in the quadratic equation of the master model.

Figures 12 and 13 show the prediction profile plots and surface plot of the predictive model. For both plots, the maximum is relatively close to the center. The center point of the graph corresponds to 310°C and 180 min which was assigned during the design of the experimental matrix as discussed earlier. This gave an insight where the optimum points would be. Using the effect estimates of the predictive model in Table 10, it was computed that the maximum bio-oil that can be produced is 70.95 ± 7.00 % by wt. at 320°C and 195 min of reaction. Effect estimates correspond to the coefficients of the equation of the model.

Methanol and 1-propanol were detected in most of the treatments but not ethanol and 2-propanol. Ethanol and 2-propanol did not co-exist in all of the samples. One possible explanation is that the peak could be for both ethanol and 2-propanol. During calibration, ethanol and 2-propanol in the chromatogram almost overlap each other. Probably, other unknown compounds present in the bio-oil may have slightly affected the elution of ethanol and 2-propanol in the column of the gas chromatograph. Thus, total ethanol and 2-propanol were considered in the analysis. The total amount of alcohols produced in all treatments did not exceed 1.6 % by wt. which is comparable to the results from the preliminary investigation. Table 11 summarizes the ANOVA results of the response surface analysis. The computed p-values suggest that there were no clear correlation between the input and the responses even if recommended data transformations were done. Therefore, the model cannot estimate the optimum conditions for maximum alcohol production.

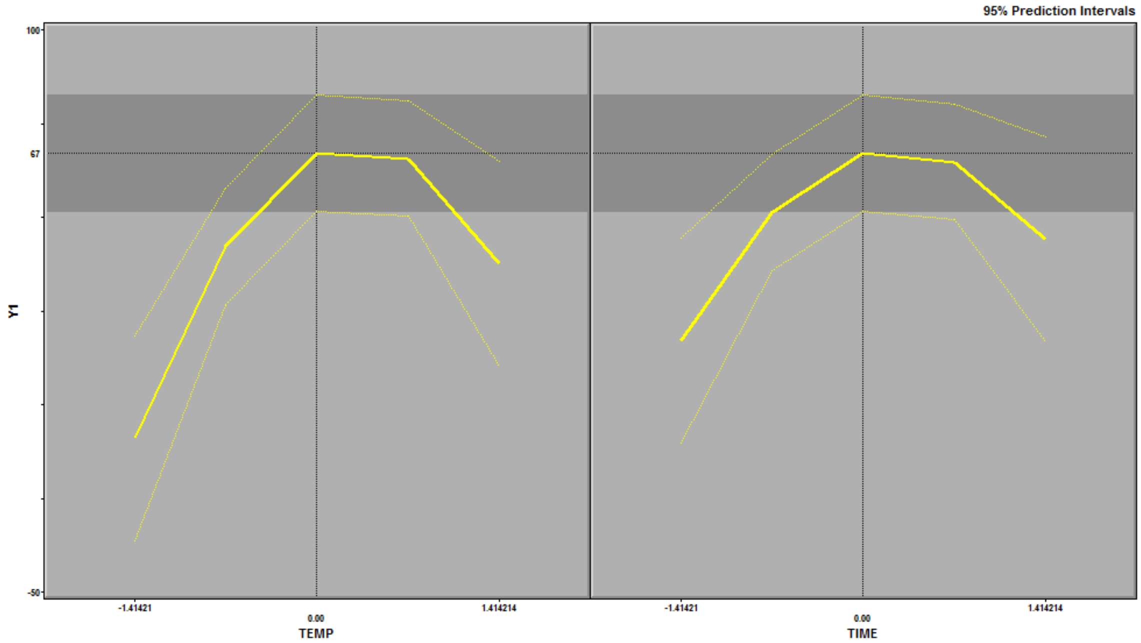

Figure 11: Prediction profile plot of the predictive model for the production of bio-oil.

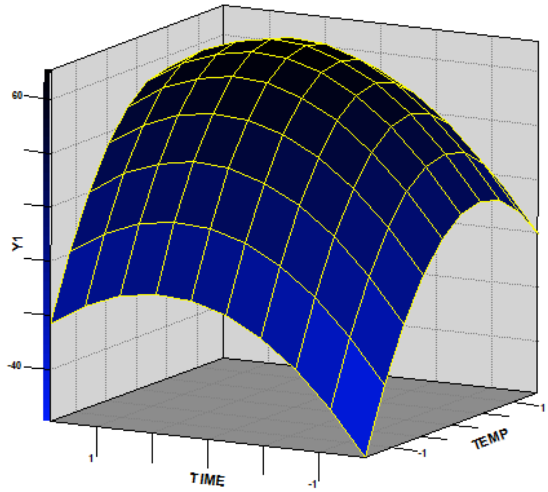

Figure 12: Surface plot of the predictive model for the production of bio-oil.

Table 11: ANOVA of the master model on the thermal conversion of glycerol to alcohols.

Source	**p-values**			
	Methanol	Ethanol and 2-propanol	1-Propanol	Total Alcohol
Temperature (T)	0.09166	0.1876	0.6042	0.1236
Time (t)	0.7995	0.4607	0.90582	0.5018
T^2	0.8663	0.8329	0.2630	0.4001
T•t	0.7950	0.5537	0.6743	0.8658
t^2	0.8385	0.5692	0.4840	0.3909

The percentages of alcohols produced relative to the total amount of glycerol varied significantly as shown in Figure 13. This variation made it difficult for the model to fit in the observed data. This also suggests that the thermochemical conversion of glycerol involves a complex set of reactions. Char formation is probably one of the reactions that contributed to the variation of the data. Even though the model failed to describe the thermochemical conversion of glycerol to alcohols, an increasing trend was observed in the percentage of alcohols in the bio-oil collected as shown in Figure 14. This suggests that minimizing the formation of char may increase the amount of alcohol produced per amount of glycerol.

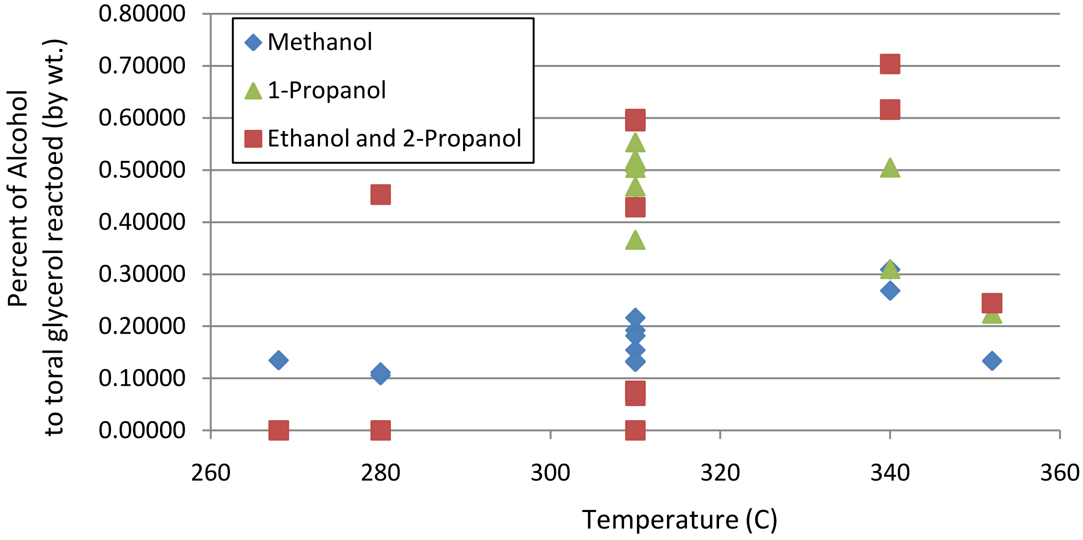

Figure 13: Plot of percent of alcohol produced against temperature.

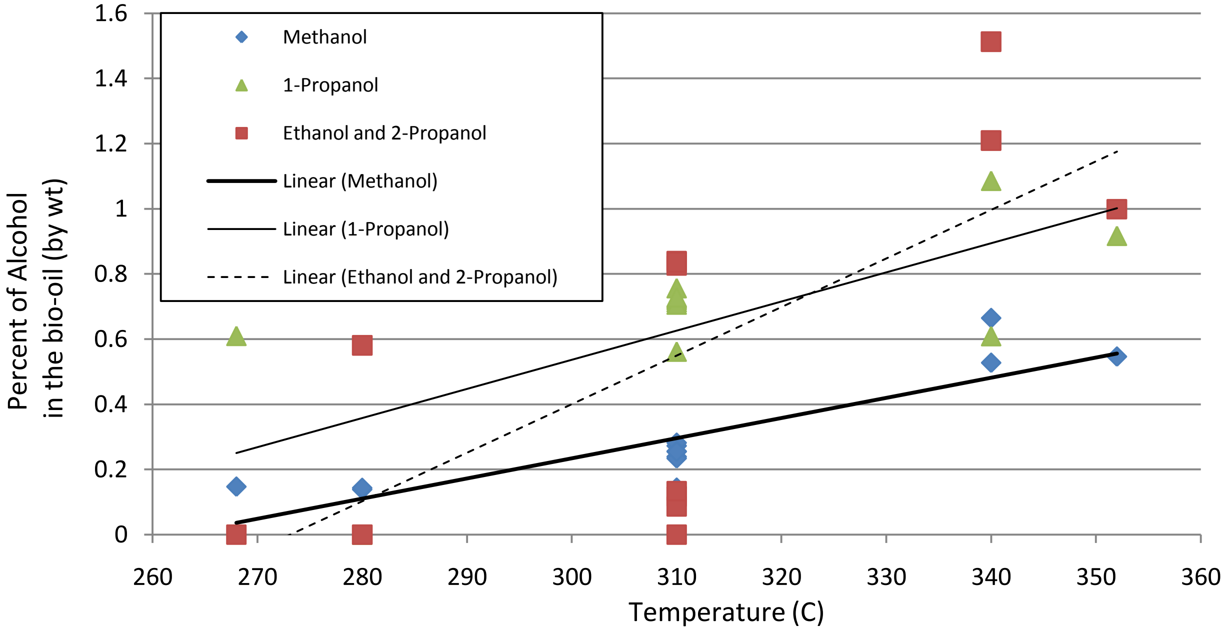

Figure 14: Plot of percentage of alcohols in the bio-oil against temperature.

Kinetics Study of the Thermochemical Process

In the response surface analysis on residual glycerol, SAS recommended a natural logarithm transformation for a better fit of the data and model (results not shown). Thus, the master model was modified to:

$$\ln(Y) = M + AX_1 + BX_2 + CX_1X_1 + DX_2X_2 + EX_1X_2$$

Results of the ANOVA on the transformed model are summarized in Table 12. According to the p-values, two parameters are not significant and were removed in the predictive model. Figures 16 and 17 show the prediction profile and surface plots generated by SAS. The amount of glycerol decreases as temperature increases and reaction time is prolonged. The trend is logarithmic similar to the first order kinetic models. In order to confirm this inference, the data collected was compared to zero-, first- and second-order kinetic models. Though the thermochemical conversion of glycerol to products is a complex set of reactions, these kinetic models were used to simplify the analysis. For the effect of temperature, Arrhenius equation was added to the kinetic models. Using Microsoft Excel Solver, it was found that the first order kinetics best describes the process. Figure 17 shows the predictive plots using the statistical model and first-order kinetics model. Both models were close to the measured data but the statistical model is limited to a certain radius of temperature and time.

Table 12: Results of the ANOVA and effect estimates of the master model and predictive model for the amount of residual glycerol

Source	Master Model		Predictive Model	
	Effect Estimate	p-value	Effect Estimate	p-value
Temperature (T)	-1.206	0.0001	-1.206	0.0001
Time (t)	-0.3469	0.005915	-0.3469	0.006916
T^2	-0.2790	0.02223	-0.2964	0.02075
T•t	-0.1913	0.1723	---	---
t^2	0.1338	0.2035	---	---

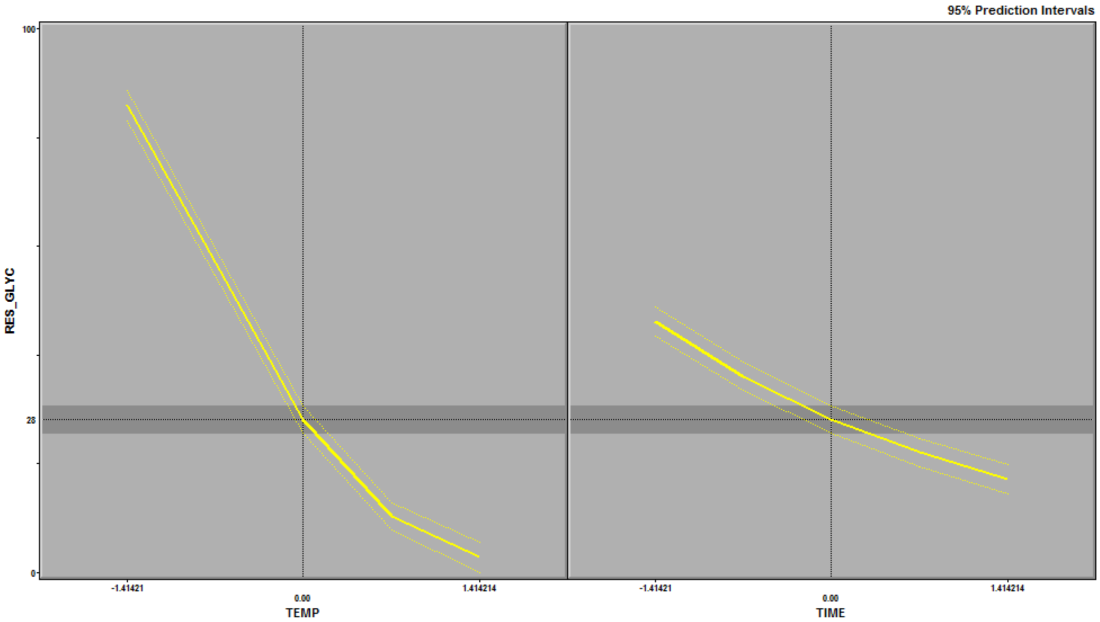

Figure 15: Prediction profile plot of the predictive model for residual glycerol.

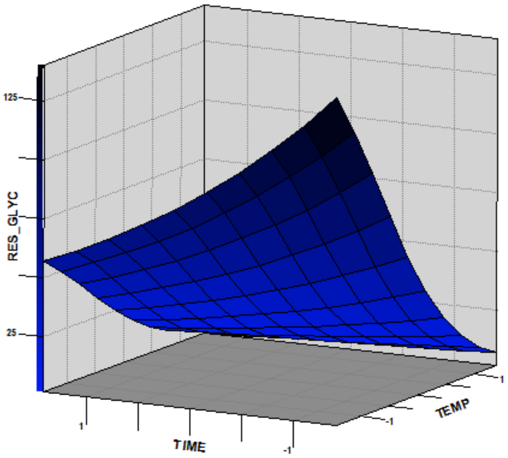

Figure 16: Surface plot of the predictive model for residual glycerol.

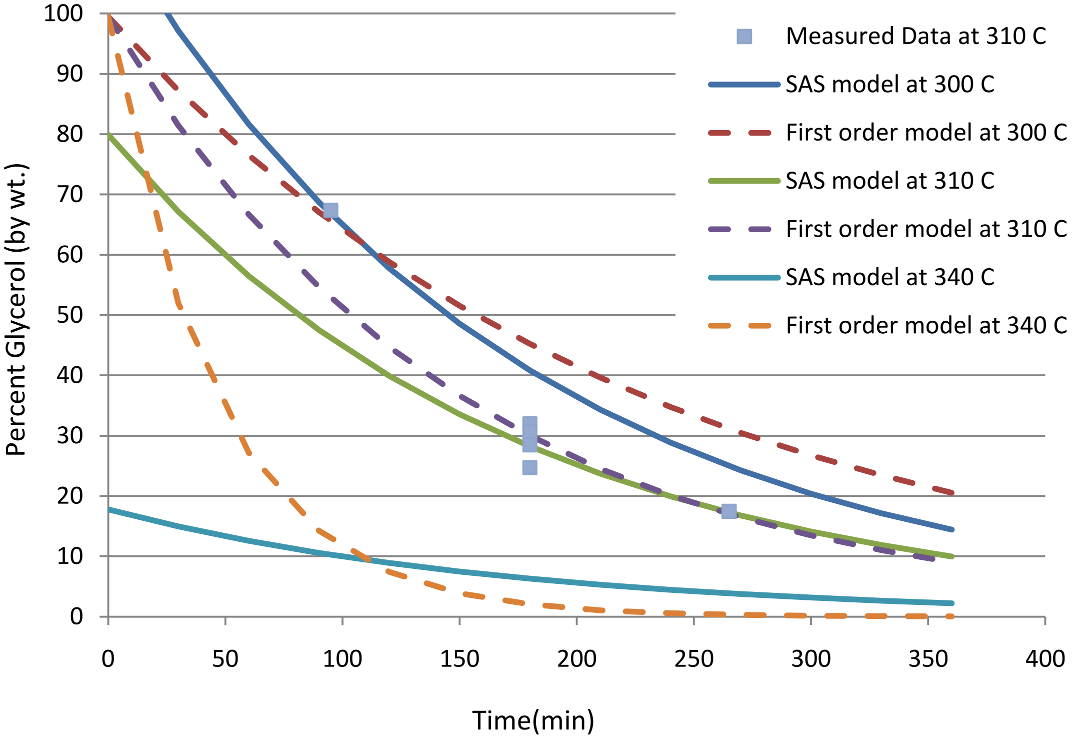

Figure 17: Plot of statistical model, first order kinetics model and the measured data at different temperatures.

Comprehensive Evaluation of the Other Process Parameters

The results from the preliminary investigation did not give enough evidence that hydrogen and carbon monoxide and its amount have significant effect on the conversion of glycerol to alcohols. However, it is difficult to deduce that the pressure and type of reducing agent has no effect on the process because the preliminary investigation gave relatively low degrees of freedom for statistical analysis. In order to have full confidence on the effect of initial pressure of the reducing agent and the type used, a full factorial experiment was conducted as shown in Table 13. The labels A and B represent the different temperature and reaction time used during the experiment. In experiment A, the reaction temperature and reaction time was set to 330°C and 180 minutes. These values were one of the levels previously used in the preliminary screening. For experiment B, temperature and reaction time was set to the optimum values determined during optimization which are 320°C and 195 minutes. In both of the experiments, approximately 100 mL of glycerol was transferred to the reactor vessel and the products were analyzed using the gas chromatograph.

Table 13: Full factorial experimental design matrixes in studying the effects of initial pressure and type of reducing agent on the thermochemical conversion of glycerol

Experiment	Treatment	Reaction Temperature and Time (°C, mins)	Initial Pressure (psig)	Reducing Agent
A	**P1**	330, 180	300	CO
	P2	330, 180	300	H_2
	P3	330, 180	0	CO
	P4	330, 180	0	H_2
B	**R1**	320, 195	300	CO
	R2	320, 195	300	H_2
	R3	320, 195	0	CO
	R4	320, 195	0	H_2

Another challenge that was encountered during preliminary investigation was the incapability of the fed-batch system to transfer glycerol from a storage vessel to the reactor instantaneously. Thus, the fed-batch system was modified. Instead of using a pump, a pressurized gas was used to push glycerol from a storage vessel to the reactor. A schematic diagram is illustrated in Figure 18. The pressure feeder is an all-purpose PARR vessel reactor. Its specifications were similar to the reactor only that it does not have an agitator assembly, pressure transducer and a cooling system. Preliminary tests using glycerol and 50 psi of nitrogen gas showed that it could transfer 100 mL of glycerol in under five seconds at room temperature. This was much faster than the previous feeding system.

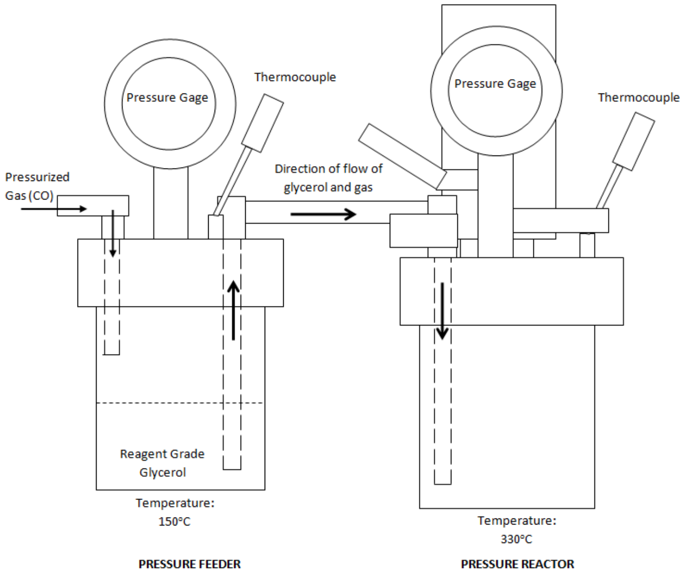

Figure 18: Schematic diagram of the pressure feeder system.

The modified feeding system was used to determine whether there would be an improvement in terms of alcohol production. As discussed earlier, repolymerization may prevent the production of alcohols during thermochemical conversion of glycerol. With this feeding system, the reactor can be preheated to the desired temperature before putting glycerol and the reducing agent to the reactor, thus, minimizing the time lag experienced during the batch experiments. The experiment has two treatments, 30 minutes and 195 minutes of reaction time. The reactor was preheated to the desired temperature of 330°C. In order to minimize the temperature difference between the reactor and the fresh glycerol, the pressure feeder was heated up to 150°C. At this temperature, glycerol will not thermochemically decompose or react. As the temperature of the reactor reaches the desired temperature, the CO gas tank was opened at 200 psig. A check valve was installed to the pipe connecting the two vessels to prevent back flow of gases. Each treatment was conducted in triplicates.

Effects of Initial Pressure and Type of Reducing Agent

Regardless of the initial pressure and type of reducing agent used, the formation of char was observed when glycerol reacted for more than 3 hours and at a temperature higher than 300°C. In the same way, the bio-oil collected has a viscosity similar to water and it is brownish in color (see Figure 19). At both initial pressures, the glycerol treated with hydrogen produced bio-oil that was relatively darker. The discrepancies in colors could be the difference on the type of chemicals produced during the reaction. However, ANOVA results suggested that except for 1-propanol, initial pressure, type of reducing agent and its combined effects did not have a significant effect on the production of bio-oil, methanol, ethanol and 2-propanol and conversion of glycerol. Initial pressure of the reducing agent was found to have affected the production of 1-propanol. In spite of the difference of percentage of 1-propanol produced, the increase at a higher pressure was only a fraction of a percent.

Modified Fed-batch Reactor System

Figure 20 shows a part of the temperature and pressure profile of one of the runs. The sudden drop in the temperature was due to the temperature difference of the preheated glycerol and the reactor. Compared with the batch experiments, it took less than 10 minutes to reach the desired reaction temperature. In addition, a portion of the glycerol was heated instantly as the glycerol entered the reactor and flowed to the sides of the reactor vessel. On the other hand, the abrupt increase in pressure means that glycerol was transferred from the pressure feeder to the reactor in a fraction of a minute. As all the glycerol was transferred, CO gas filled up the two vessels and equilibrated at 200 psig which was the set tank pressure. During the reaction, the pressure of the reactor continued to increase since volatile compounds were formed. The check valve prevented the back flow of these gases to the pressure feeder.

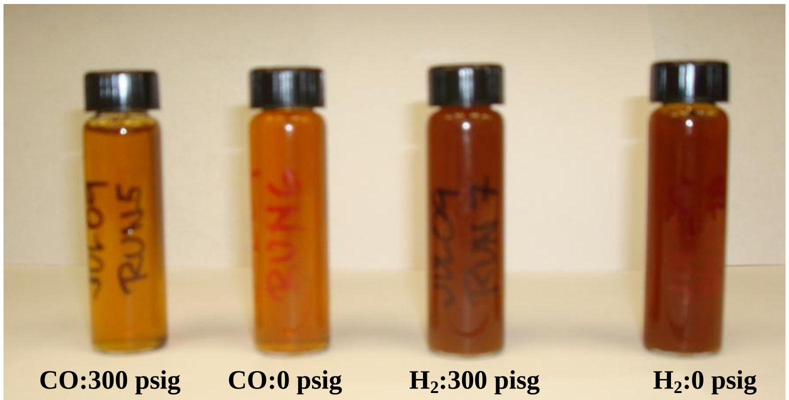

Figure 19: Glycerol after thermochemical conversion at different pressures and using different reducing agents.

For both treatments, there were no significant improvements in alcohol production. The amount of methanol, ethanol, propanol in the samples collected were still less than a percent (by weight) It was also observed that at 30 minutes of reaction time, char formation was minimal and 52% (by wt) of glycerol was still in the sample. This suggests that thermochemical conversion occurs at a very slow rate at temperatures from 300 to 350°C.

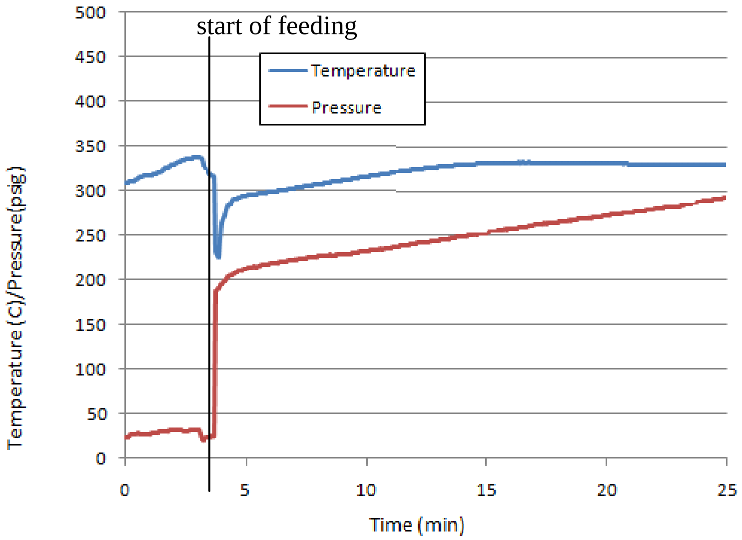

Figure 20: Temperature and pressure profiles as glycerol was injected in the reactor using the pressure feeder.

CONCLUSIONS

In the determination of ethanol, methanol, propanol and glycerol, the methodology developed using gas chromatography was able to detect all the target compounds. Statistical analysis also showed that the results in the gas chromatograph did not vary from day to day. Thus, the methodology can be used to simultaneously detect ethanol, methanol, propanol and glycerol in samples.

Initial pressure of the reducing agent, reaction temperature, type of reducing agent and time of reaction were identified to be important in the thermochemical conversion of glycerol to alcohols. This was supported by the observation from the experiments conducted which showed that glycerol was converted into bio-oil and char with the presence of carbon monoxide or hydrogen at above 300°C and longer than an hour of reaction. The characteristics of the bio-oil collected suggest that glycerol have been converted to a mixture of compounds that have viscosity similar to water. The increase in the pressure at constant temperature during the reaction implies that the compounds formed were also volatile or semi-volatile.

Statistical analysis confirmed that temperature and time of reaction significantly affected the thermochemical conversion of glycerol. Through response surface analysis, it was found that the optimum conditions for maximizing the ratio of bio-oil to char is at temperature and reaction time of 320°C and 195 minutes, respectively. However, there was no clear relationship between these two parameters with respect to the production of alcohols. The lack of fit of the predicted model used for response surface analysis was due to the great variation of the data. This variation suggests that the thermochemical conversion of glycerol to alcohols might have been significantly influenced by other uncontrollable factors. Formation of different intermediates during the reaction may have contributed to the significant variation of the observed data. This also implies that the thermochemical conversion of glycerol involves a complex set of reactions. Nevertheless, a simple first-order kinetics model was able to describe the conversion of glycerol to the different products.

The results on the thorough analysis on the effects of other two parameters could conclude that initial pressure and type of reducing agent do not affect the amount of bio-oil and alcohols produced.

RECOMMENDATIONS AND FUTURE WORK

The results of the experiment gave sufficient evidence that temperature and time of reaction affect the thermochemical conversion of glycerol. In addition, the process could produce methanol, ethanol and propanol from glycerol. However, further studies should be done to improve the efficiency of the process. The possible reasons for not being able to produce more than 2% of alcohols are (1) the reactions did not go by the pathway expected, (2) the alcohols produced decomposed into simpler compounds like water and char (3) and the alcohols produced reacted with other compounds to form bigger compounds.

An investigation on the effect of metal catalysts is recommended for further research. Metal catalysts have been found to affect the production of allyl alcohols from glycerol and the hydrogenation process in producing alcohols. Metal catalysts may favor the production of alcohols instead of other compounds in the thermochemical conversion of glycerol.

A study on reactive distillation is likewise recommended for future research. Reactive distillation would minimize further decomposition of the alcohols produced in the reactions. Using a catalyst and this system may improve the production of alcohols from thermochemical conversion of glycerol significantly.

ACKNOWLEDGEMENT

The National Institute of Advanced Transportation Technologies (NIATT) is gratefully acknowledged for its financial support through the University Technology Centers (UTC) fund. Major researchers in this project include Dr. B. Brian (PI), Randy L. Maglinao, Graduate Research Assistant, Dr. Joe Thompson, Engineering Support Scientist. Undergraduate researchers of Sushant Kshetri and Yao Zhang are also gratefully acknowledged for their assistance on this project.